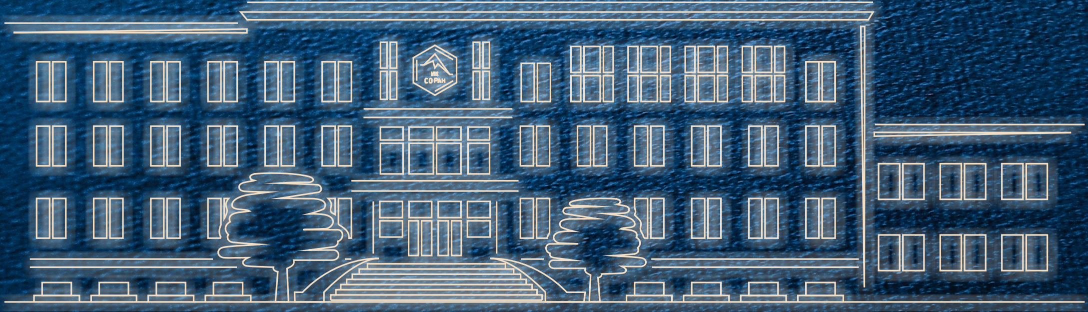
April 19-21, 2017
Novosibirsk, Russia

IV Scientific Conference
BORESKOV READINGS

dedicated to the 110th anniversary of Academician Georgii K. Boreskov

ABSTRACTS

Novosibirsk-2017



Boreskov Institute of Catalysis SB RAS, Russia
Zelinsky Institute of Organic Chemistry RAS, Moscow, Russia

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УДК 541.128+542.97+544.4+66.09
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- Surface oxygen species: local structure, electronic state, and reactivity
- Structural sensitivity, size effects, and single atom catalysis
- Mechanism of oxidative reactions
- From reaction kinetics to industrial innovation processes

The Conference is accompanied by the School-Symposium of young scientists "*In situ* and *operando* studies of the catalytic reactions"

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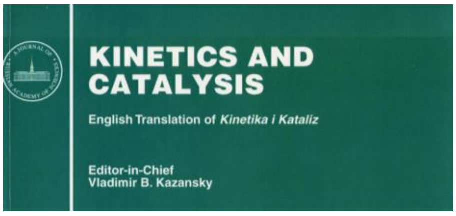
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PLENARY LECTURES

PL-1

Heterogeneous catalysis for production of commodity chemicals from renewable feedstocks

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Renewable, carbohydrate-based raw materials are particularly well suited to the production of chemicals. Attractive features such as natural abundance, oxygen functionality and low prices make then attractive replacements for oil-based feedstocks. Many valuable commodity chemicals (for example, diols, dicarboxylic acids and diamines), can in principle be produced from these raw materials at competitive productions costs [1].

Heterogeneous catalysts will undoubtedly play an important role in this emerging industry [2], however the catalyst transformations of polar, non-volatile feedstocks present new challenges that must be overcome to enable industrial applications. In particular, solid catalysts must function effectively in rather aggressive environments such as aqueous or acidic solutions.

In this lecture some examples of the application of heterogeneous catalysts for the transformation of renewable raw materials to commodity chemicals will be considered. Emphasis will be given to the developments undertaken by Rennovia to commercialize novel catalytic process technology [3, 4].

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PL-2

Catalysis by design: well-defined single-site heterogeneous catalysts via surface organometallic chemistry

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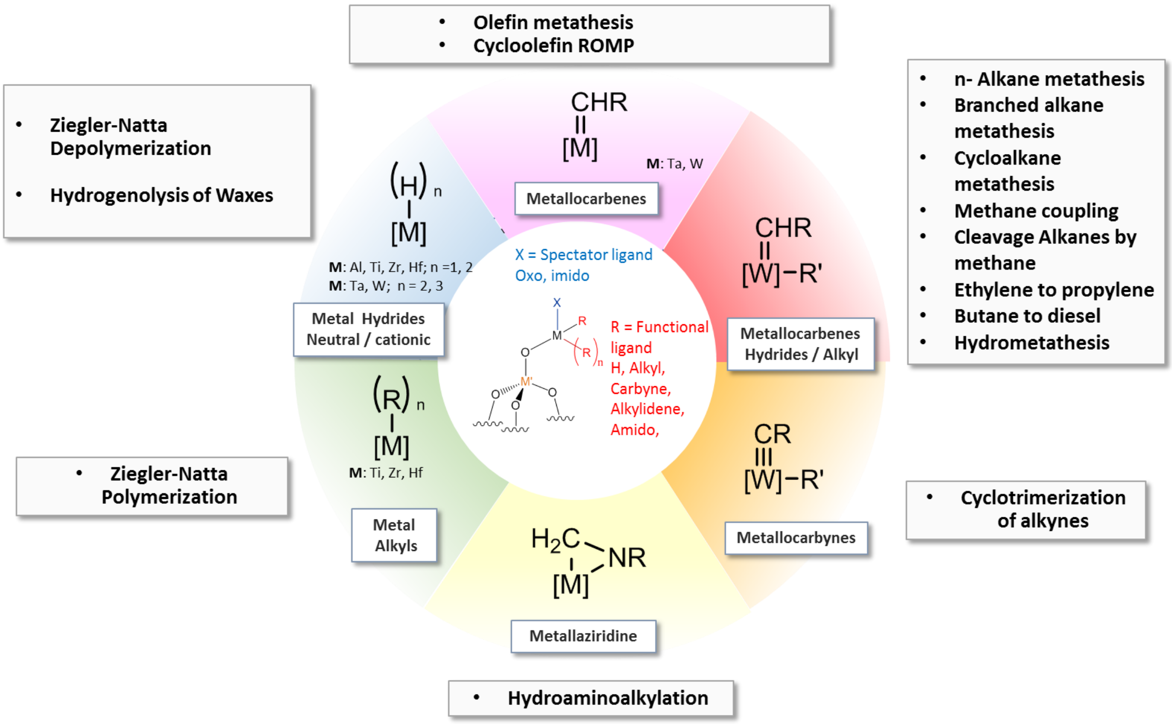
Heterogeneous catalysis, a field important industrially and scientifically, is increasingly seeking and refining strategies to render itself more predictable. The main issue is due to the nature and the population of catalytically active sites. Their number is generally very low, their “acid strengths” or “redox properties” is not homogeneous, and the material may display related yet inactive sites on the same material. In many heterogeneous catalysts, the discovery of a structure-activity relationship is at best challenging. One possible solution passes by generating single-site catalysts in which most of, if not all, the sites are structurally identical. Within this context and using the right tools, the catalyst structure can be well-defined, that is elucidated to reach a molecular understanding. It is then feasible to understand structure-activity relationship and to develop predictable heterogeneous catalysis. Single-site well-defined heterogeneous catalysts can be prepared using Surface Organometallic Chemistry. This approach operates by reacting organometallic compounds with surfaces of highly divided oxides (or of metals nano particles). This strategy has a solid track record to reveal structure-activity relationship to the extent that it is becoming now quite predictable. Almost all the elements of the periodical table have been grafted on surfaces of oxides (from simple oxides such as silica or alumina to more sophisticated materials regarding composition or porosity).

Considering catalytic hydrocarbon transformations, heterogeneous catalysis outcome may now be predicted based on existing mechanistic proposition and the rules of molecular chemistry (organometallic, organic, supramolecular) associated to concepts of surface sciences. A thorough characterization of the grafted metal centers must be carried out using tools spanning from molecular organometallic or surface chemistry. By selecting metal and its ligand set (or support taken as a X, L, Z ligands in the Green formalism), the catalyst can be designed and generated by grafting organometallic precursors with functional groups suitable to targeted transformation. Subtles transformations are necessary to go from a precatalyst stage to the real catalytic intermediates. The coordination sphere necessary for any catalytic reaction involving paraffins, olefins, alkynes aso can now be predicted. This catalysis occurs via successive elementary steps occurring on surface organometallic intermediates. Only their most complete understanding can allow to develop catalytic reactions with the highest possible selectivity, activity and lifetime. In this lecture we will examine the results of SOMC for hydrocarbon transformations on oxide surfaces bearing metals of group IV - VIII. The silica-supported catalyst are exhibiting remarkable performances for Ziegler Natta polymerization and depolymerization, low temperature hydrogenolysis of alkanes, waxes, metathesis of alkanes, cycloalkanes, metathesis alkenes,

PL-2

Catalysis by design: well-defined single-site heterogeneous catalysts via surface organometallic chemistry



- **Olefin metathesis**
- **Cycloolefin ROMP**

- **Ziegler-Natta Depolymerization**
- **Hydrogenolysis of Waxes**

- **n- Alkane metathesis**
- **Branched alkane metathesis**
- **Cycloalkane metathesis**
- **Methane coupling**
- **Cleavage Alkanes by methane**
- **Ethylene to propylene**
- **Butane to diesel**
- **Hydrometathesis**

- **Ziegler-Natta Polymerization**

- **Cyclotrimerization of alkynes**

- **Hydroaminoalkylation**

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PL-3

OXYGEN ACTIVATION ON METAL-OXIDE SURFACES

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Metal oxide based materials are widely used as catalysts in many processes belonging to very different types of chemical reactions such as oxidation, dehydrogenation, dehydrocyclization, or dehydrocondensation. In all these processes the most important role is played by surface oxygen centers.

In the following oxygen activation on transition metal surfaces (V_2O_5, MoO_3), on metal particles dispersed in a zeolite (Pd-MOR) and on selected tungsten and molybdenum polyanions ($PW_{11}CoO_{39}$ and $H_5PMo_{11}CoO_{39}$) will be discussed by means of DFT approach. Both local (cluster model, TURBOMOLE code) and nonlocal (periodical, VASP code) models will be applied.

Reduction of systems by formation of oxygen vacancy at structurally different oxygen sites are studied by removing these oxygen spieces. In addition in case of selected systems hydrogen assisted vacancy formation is presented. Next, re-oxidation process is discussed by adsorbing molecular oxygen at these vacancies. For heteropolyanions the exchange of solvent ligand by reactive oxygen species will be presented.

The energetics of vacancy formation strongly depend on type oxygen site as well as on type of process leading to the formation of vacancy. Molecular oxygen always stabilizes at surface vacancy leading to surfaces that are richer in oxygen in comparison to pure surfaces.

PL-4

Selective oxidation and reaction mechanism over crystalline Mo-based oxide catalyst

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Development of new complex metal oxides having structural complexity suitable for solid-state catalysis is of great importance in fundamental catalysis researches and practical application. However, examples of these materials are not many. Herein, two types of new complex metal oxides with novel crystal structures and remarkable catalytic properties for ethane oxidation and aldehyde oxidation in gas-phase will be introduced.

The first example is a crystalline Mo_3VOx with heptagonal channel pores. Polyoxometalates(POMs) were utilized as building block donors for construction of microporous complex metal oxides. Assembly of POM units of $[Mo_6O_{21}]$ forms orthorhombic Mo_3VO_x and trigonal Mo_3VO_x. These crystalline Mo_3VO_x catalysts show extremely high activity for the selective oxidation of ethane. Ethane molecule can enter the heptagonal channel micropore and the ethane oxidation takes place. Molecular oxygen is activated at oxygen vacancies between Mo and V in the pentamer near the heptagonal channel to be peroxo-species that can abstract hydrogen from ethane in the channel as illustrated in Figure 1 [1]. The present work demonstrates the role of micropore in the selective oxidation of ethane with crystal level understanding.

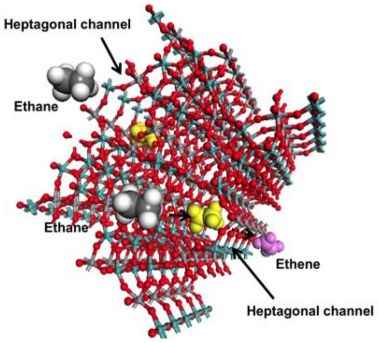

Figure 1. Ethane oxidation on Mo_3VOx catalysts

The second example is a porous 3D framework POM shown in Figure 2. ε-isomer of Keggin POM was another building block for crystalline microporous complex metal oxides[2]. Assembly of ε-Keggin POMs with octahedra linkers produces microporous complex metal oxides. This porous POM shows zeolite-like properties. The micropores of the materials are opened by removing water and ammonium cations in the cages by calcination. CH_4 and C_2H_6 can be adsorbed in the micropores in the materials. This material was demonstrated as a catalyst for gas-phase oxidation of methacrolein to methacrylic acid.

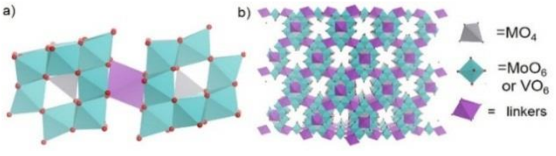

Figure 2. ε-Keggin POM with metal ion linker(a) and framework of ε-Keggin POM-based porous materials(b)

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KEYNOTE LECTURES

KL-1

Catalysis using new nanomaterial catalysts

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Catalysis is of crucial importance for the manufacture of the goods and infrastructure necessary for the effective wellbeing of society. Catalysis, and in particular selective redox catalysis, continues to play a key role in the manufacture of chemical intermediates and there is a continuing requirement to design new effective redox catalysts. For example, the identification that gold in nanoparticulate form is an exceptionally effective redox catalyst has paved the way for a new class of active catalysts. Alloying gold with other metals can enhance the activity and these catalysts are effective for the oxidation of alcohols and hydrocarbons as well as the direct synthesis of hydrogen peroxide. In this presentation the use of gold as a key component of catalysts for the direct synthesis of hydrogen peroxide, which is a hydrogenation reaction, and the oxidation of alcohols will be discussed. The synthesis of active catalysts will be described as well as their characterization. Aspects of the latest research on topics involving new nanomaterials will also be presented.

KL-2

Recent advances in petrochemical technologies for olefin and aromatics production

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This presentation will discuss the most advanced new emerging technologies for light olefin and aromatics production. The landscape for industrial production of olefins is changing rapidly with intense commercialization of Methanol-to-Olefins (MTO) and on-purpose propane dehydrogenation technology, e.g. Oleflex^{TM}. The dehydrogenation of propane to produce propylene has become a critical technology to fill the propylene shortage, which is increasing due to the portion of steam crackers now using inexpensive ethane feedstock [1]. This trend is expected to continue through the next decade. The demand for p-xylene will continue to grow rapidly with production exceeding 80 million tons by 2024 [2]. The transalkylation of toluene with heavier aromatics like trimethylbenzene is a key process to increase the xylene yield from aromatics complexes. Transalkylation accounts for 60% of all xylenes produced.

Advanced dehydrogenation multi-metallic catalysts are prepared which are sub-nanometer and provide superior activity, selectivity, stability and regenerability which ensures long life and superior process economics [3]. We discuss the critical factors for advanced catalysts for on purpose light paraffin dehydrogenation catalysts as well as process improvements. We have used advanced AC-STEM to understand Pt catalyst structure-function relationship at <1 nm.

Over the decade, major improvements in aromatics transalkylation have been made in catalyst activity and stability, mainly through the introduction of a metal function, secondary zeolites and improvements in the properties of the mordenite. As part of UOP's ongoing New Materials program, a zeolite with the MOR framework and crystal size significantly smaller than current state-of-the-art mordenites was synthesized. This material, designated UZM-14 (for UOP Zeolytic Material #14), was formulated in an aromatics transalkylation catalyst and compared to reference catalysts with commercially available mordenite. The catalytic results will be shown and correlated crystal length in the pore direction by advanced x-ray diffraction techniques.

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KL-3

Catalysts for synthetic bio-butadiene: from industrial application to reaction mechanism

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The production of "bio-olefins" is currently one of the most investigated topics in the field of the valorization of biomass for the production of chemicals, as demonstrated by the impressive number of papers and patents issued on this topic during recent years [1]. In this context, several alternatives are being considered for the synthesis of butadiene, such as bio-butandiol dehydration, direct fermentation routes, or the one-step transformation of bio-ethanol, the so-called *Lebedev* process, developed in Russia during the 1930's. Various catalysts have been proposed for this reaction, and many of them include MgO and SiO_2 as the main components, besides additional promoters which are aimed at facilitating the dehydrogenation of the alcohol to acetaldehyde, the first step of the complex reaction mechanism.

We recently reported that indeed the mechanism for the formation of butadiene does not involve the aldol condensation of the in-situ formed acetaldehyde and the H-transfer from ethanol to the intermediate crotonaldehyde, but instead consists of a direct reaction between acetaldehyde and ethanol to form crotyl alcohol, which is then dehydrated to butadiene [2]. We also investigated on the reasons for the superior performance shown by MgO/SiO_2 catalysts [3], and on the role of Ga^{3+} as a promoter for the reaction [4].

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Methane dehydroaromatization - new insights and opportunities

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Non-oxidative methane dehydroaromatization (MDA) over zeolite-supported Mo-carbides continues to be one of the most promising options for directly converting natural gas into aromatic hydrocarbons and hydrogen. Commercialization is hampered by rapid coking deactivation. Here, we present two novel ways to mitigate formation of coke at reaction temperature. First, pulsing small amounts of oxygen in the feed can selectively combust the coke. Second, we demonstrate that lowering the Mo content of Mo-ZSM-5 results in much improved hydrothermal stability, to the extent that the zeolite catalyst can be regenerated at reaction temperature in (artificial) air.

Supplying small pulses of oxygen to a continuous methane feed over a fixed catalyst bed containing Mo/HZSM-5 allows greatly stabilizing catalytic performance in methane dehydroaromatization at 700 °C (Fig. 1, left). Using ^{13}C-labelled methane, we demonstrate that oxygen first reacts with Mo-carbides to produce Mo-oxide, which is the catalyst for coke combustion. There is only a small contribution of the combustion of gaseous reactant and products. The main side-product of the pulsed combustion strategy is valuable synthesis gas. We also systematically explored the air stability at high temperature (550-700 °C) of Mo/ZSM-5. At low Mo loading (1-2 wt % Mo), Mo is predominantly dispersed in the zeolite micropores as cationic Mo-oxo-complexes. At higher loading, most of the initially aggregated Mo-oxide at the external surface are dispersed into the micropores when the temperature is increased above 600 °C, resulting in reaction of mobile MoO_3 species with framework Al and irreversible damage to the zeolite framework. High stability of Mo/HZSM-5 with low Mo loading (< 2 wt%) allows operating the catalyst in a stable manner using an isothermal (700 °C) reaction – air regeneration, whereas conventional 5 wt % Mo/HZSM-5 rapidly lost its activity, an optimized 2 wt % Mo/HZSM-5 catalyst retained more than 50 % of its initial activity after 1 week (100 cycles; Fig. 1, right).

KL-4

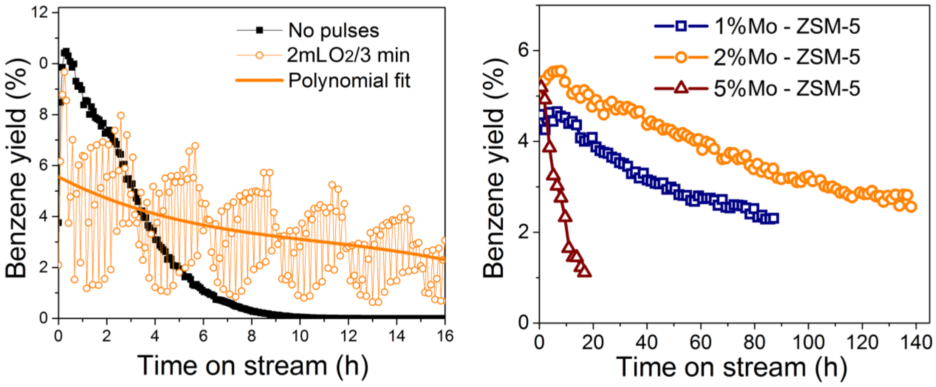

Figure 1. Comparison of different MDA modes. Left: typical oxygen-free MDA run over 5 % Mo/HZSM-5 at 700 °C, atm. pressure a (black squares); test with pulsing 2 mL oxygen every 3 minutes into the methane feed (ginger circles). Right: isothermal reaction-regeneration MDA cycling

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KL-5

Synchrotron, operando and DFT studies of the CuO_x/CeO_2 CO-PROX catalyst: surface structure effects

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In CuO_x/CeO_2 catalysts used in the CO-PROX reaction, borderline sites at the CuO_x-CeO_2 interface are assumed to be key active centres; thus changing its structure could have a significant effect. We verified this recently, detecting a selectivity improvement (retarding of H_2O formation) when the CeO_2 support has nanocube (NC) shape, exposing mainly the less stable (001) surface [1], compared with nanosphere (NS) shape. Then we have carried out synchrotron studies, including XPS measurements under gas pressure [2], to verify the proposed model, complementing it with DFT calculations and HR-TEM data.

The results, both experimental and theoretical, give further proof that the surface CuOx entities are more hard to reduce to zerovalent Cu (the species more easily activating H_2), due to a stronger wetting interaction between those entities and the (001) surface. In addition, some unusual XPS core level shifts are detected which on the basis of their DFT modelling could be fingerprint of specific Cu centres at the interface with ceria.

Acknowledgement:

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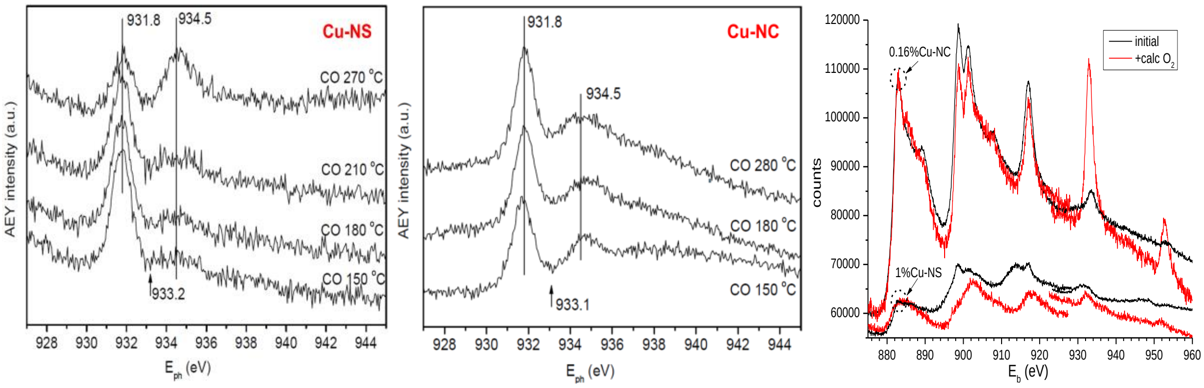

Fig. 1. Left & centre: Cu L_3 XANES (with Cu LMM Auger detection) of CuO_x/CeO_2 under 0.5 mbar CO at increasing Ts. Right: effect of calcinations on Cu and Ce XPS intensities in CuO_x/CeO_2

KL-6

What you see is (not) what you get – why we need operando spectroscopy to unravel the state of active sites formed from precursors

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A catalyst is a substance that enhances the rate of a chemical reaction without being consumed itself. This term coined by Wilhelm Ostwald in 1895, however, does not mean that a catalyst does not undergo changes during catalysis. In fact, most of the catalysts in both homogeneous and heterogeneous catalysis experience severe changes and what you see in the as-prepared precursor is not what you get in the active catalyst. Moreover, the structure of the active sites is frequently not preserved upon stopping the catalytic reaction. Thus, the only way to identify the real nature of the active sites in a catalytic reaction is using operando spectroscopy for monitoring precursor-to-catalyst transformation under reaction conditions. This will be demonstrated by two examples chosen from heterogeneous catalysis, namely butene dimerization with supported nickel catalysts and electrocatalytic oxygen evolution reaction (OER) with mixed CoNi and CoCu oxide catalysts.

Supported Ni/SiO$_2$-Al$_2$O$_3$ catalysts with Ni loadings below 0.5 % are active and selective in butene dimerization. In their as-prepared state they contain exclusively Ni(I) single sites which, however, change their valence state and loose dispersion, depending on the total reaction pressure. These changes are visualized by a combination of *operando* EPR and *in situ* XANES/EXAFS at 350 K and a total pressure of 1 – 16 bar. Single Ni^{I}/Ni^{II} shuttles are formed as active sites at elevated pressure, whereby the conversion of initial Ni^{I} to Ni^{II} by oxidative addition of butene is faster than the re-reduction of Ni^{II} to Ni^{I} by reductive elimination of the C8 product, rendering the equilibrium percentage of Ni^{I} much smaller than in the catalyst precursor. At $p \leq 2$ bar, Ni^{I} single sites form inactive Ni^{0} aggregates which is suppressed at higher pressure (≈ 12 bar).

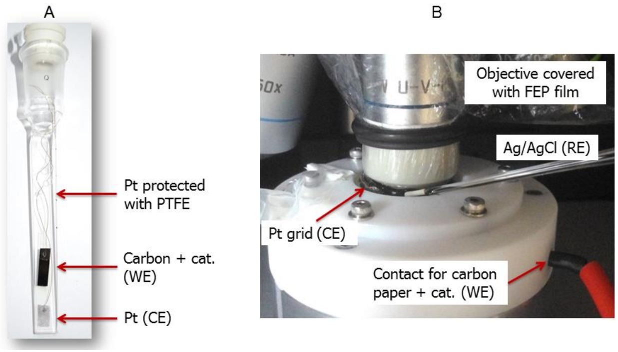

Fig. 1. Spectroelectrochemical cells for in situ EPR (A) and in situ Raman spectroscopy (B)

In situ Raman and *in situ* EPR spectroscopy have been used to investigate the metamorphosis of mixed spinel-type cobalt nickel and cobalt copper oxides in the electrocatalytic oxygen evolution reaction (OER) from water. All experiments were carried out in home-made spectroelectrochemical cells using 0.1M KOH as electrolyte. Depending on the annealing conditions of the catalyst precursors, different OER activities were obtained and correlated with the spectroscopically detected features. In Co/Ni oxides γ- and/or β-NiO(OH) are formed at the onset potential for OER, whereby a higher percentage of β-NiO(OH) accounts for higher activity. In Co/Cu catalysts the partial dissolution of Cu(II) led to the formation of a Co-enriched highly disordered or amorphous oxide/hydroxide phase that boosts activity.

KL-7

Catalysis and energetics: experience of the Boreskov Institute of Catalysis

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The presentation concerns the experience of the Boreskov Institute of Catalysis (BIC) in the development of catalysts and catalytic technologies for the production of high-quality fuel from the traditional raw hydrocarbons, as well as for processing of associated petroleum gas and application of catalytic processes for energetics of the future. Specifically, under discussion are BIC's proprietary ecologically sound coal-burning thermal power plants based on catalytic burning of different, including low-calorific, fuels; synthesis of high-quality fuel from renewable plant resources; application of reversible thermocatalytic processes for high-efficient direct conversion of nuclear and concentrated solar energy into chemical energy.

Under discussion are problems of quantum transformation of solar-to-chemical energy *via* creation of artificial photocatalytic systems mimicking the natural photosynthesis in plants and bacteria. The BIC experience of a considerable improvement in the utilization of motor fuel through its pre-conversion to synthesis gas using car-board catalytic processors is discussed, too. Another example under consideration is the possibility of efficient recuperation of low-potential heat through its accumulation by composite materials such as selective water sorbents.

KL-8

Perspective catalytic reactions for production hydrocarbons components fuels and alcohols C_4-C_8 based on bio oxygenates

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Keywords: alcohols, rapeseed oil, catalysts, structure, bimetallic active components, catalytic activity and selectivity, hydrocarbon fuel, chemicals

Introduction

Ethanol, 2-methylpropanol-1, 3-methylbutanol-1, mixture of fermentation organic products, glycerol and rapeseed oil are known to give rise bio-fuel components under hydro-deoxygenation conditions. Selective conversions of bio-substrates into alkanes, olefins, aromatics and naphthenic hydrocarbons components of gasoline and diesel fractions as well as n-butanol and 2-dymethylpentanol-2 were observed in this paper. Commercial and original catalysts based on alumina and zeolite supports containing nanosized bimetallic active components of I, II, V- VIII groups have been tested in these reactions.

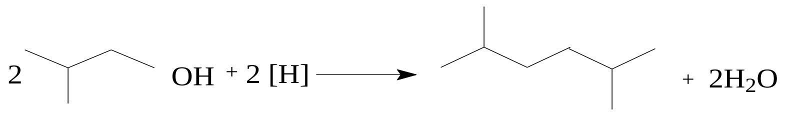
Results and discussion

Ethanol conversion to fraction of alkanes C_5-C_{10+} at 300-350 °C in inert atmosphere was found to be catalyzed with industrial Pt/Al_2O_3 catalyst after special pre-activation as in (1)[1]**:**

$$mC_nH_{2n+1}OH + H_2 \rightarrow C_{mn}H_{2mn+2} + mH_2O, \qquad (1)$$

were $n \geq 1$; $m \geq 2$

2-methylpropanol-1 and 3-methylbutanol-1 were converted into 2,5-dimethylhexane and 2,7-dimethyloctane, respectively as in (2):



(2)

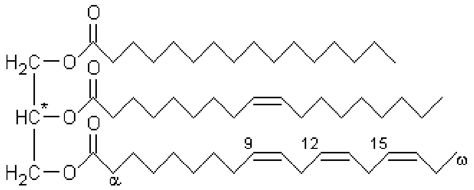
Cross-condensation of ethanol with acetone, bio alcohols, and glycerol in the presence of Pt/Al_2O_3 и [W(Ta)-Re]-catalytic systems leading toward the formation of new hydrocarbons with enlarged and branched carbon skeleton was observed (3):

$$C_2H_5OH+C_3H_5(OH)_3 \longrightarrow C_5 - C_{12+} \text{ (alkanes, olefins)} + nH_2O \qquad (3)$$

Hydrogen consumed in product forming reactions 1-3 originated from in-situ in reaction zone via parallel reaction dehydrogenation and aromatization of initial alcohol.

Ethanol/bio-alcohols transformation is multivariate reaction and mainly depends on catalyst composition: 1) in the presence of modified platinum-contained catalyst reaction involves oligomerization of ethylene as intermediate; 2) aldol condensation is the main stage of hydrocarbons forming in the presence of $W(Ta)\text{-}Re/Al_2O_3$ and $Pd\text{-}Zn/Al_2O_3$ catalysts; 3) alkane-aromatic hydrocarbons forming according to well-known “hydrocarbon pool” mechanism in the presence of Pd-Zn/ZSM-5 catalyst[2].

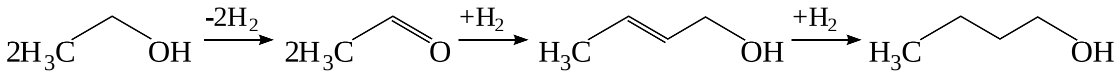
In the presence of original Pt-Sn/Al_2O_3 catalyst at 400-420 °C and 30 atm H_2 rapeseed oil was unexpectedly found to yield dominantly narrow alkane-olefins C_3, C_{18} and H_2O (4)[3]:



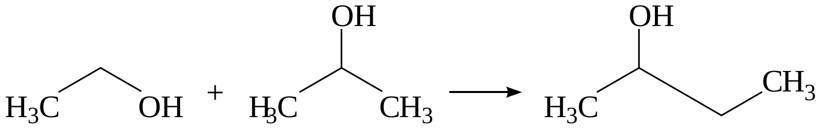
$$\longrightarrow C_3 + C_{18} + nH_2O \quad (4)$$

The total selectivity of direct deoxygenation reaches up to 99 %. The yield of C_3 and C_{18} hydrocarbons in the products was ~ 92 %. The total yield of C_1 and C_2 hydrocarbons as well as carbon oxides does not exceed 0,5-0,7 % that provides minimization of the carbon loss in the process of rapeseed oil deoxygenation.

High activity (70 %) and selectivity (60-70 %) in reactions of β-alkylation of ethanol to n-butanol and cross-alkylation of ethanol by isopropanol-2 to iso-pentanol-2 was reached in the presence of nanosize bimetallic catalysts such as Au-Ni; Au-Cu and Au-Ag forming on the surface of γ-Al_2O_3 (5,6)[4,5].



(5)



(6)

Structure and evolution of the catalyst active sites were studied using TP-desorption of molecules-probes, XAFS, XPS, X-Ray and TEM HR. Relationships between structure of active components and catalytic activity of catalysts are discussed.

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KL-9

Oxidative desulfurization of diesel fractions: From mechanistic studies to prospective industrial technology

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Boreskov G.K., as one of the recognized international leaders of catalysis, made substantial input in oxidative catalysis, both in fundamental studies of reaction mechanisms and in development of large-scale industrial technologies [1, 2].

The gas phase oxidative desulfurization (ODS) of motor fuels with air or oxygen, initially proposed for desulfurizing petroleum fractions, is widely investigated to date as a new promising technology for removal of 4,6-dimethyldibenzothiophene (DMDBT) and other alkyl-substituted dibenzothiophenes (DBT) [3]. The DBT family is well-known to accumulate in high-boiling fractions, and they are refractory to hydrodesulfurization reactions.

Thirty catalysts based on Cr, Fe, Mo, Cu, Ce, Zn, and Al oxides or their mixtures have been screened in the gas-phase oxidative desulfurization of simulated fuels containing DMDS, thiophene, DBT or DMDBT by air [4,5].

We studied in detail ODS of model heterocyclic sulfur-compounds as well as straight-run diesel fuel (1 wt.% S) in gas-vapor phase over CuZnAl-O catalysts, unmodified [4,5] and modified by cation/anion additives [6,7]. The molar ratio O_2/S, LHSV, GHSV and temperature were varied within a wide range for the purpose for increasing of sulfur removal efficiency. According to DTA-TG-MS, FTIR and XPS data, at 300-500 °C ODS proceeds via the stage of adsorption of sulfur containing molecules, followed by their destruction and evolution of SO_2 into the gas phase. In case of strong interaction of sulfur-containing molecules with the catalyst active sites the accumulation of sulfur on the catalyst surface takes place in the form of metal sulfides, polysulfides and sulfates. The modification of CuZnAl-O catalyst by Mo and B oxides allowed us to improve its stability [6, 7].

Based on the accomplished fundamental research, several schemes of the developed processes, partly in combination with traditional HDS were proposed for industrial implementation and protected by US and international patents [8].

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KL-10

Based by G. Boreskov Department at Mendeleev University since 1949 up to now

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In February, 1949 according to the order of the Government of the USSR at the Moscow D. Mendeleev Institute of Chemical Technology (MCTI) the Engineering Physical Chemistry Faculty started working. It is included the two graduating departments; one of them was intended for training specialists in the field of technology of separation and application of light element isotopes. Director of MCTI of that time professor N.M. Zhavoronkov attracted Dr. Sci. Eng. G.K. Boreskov (being the Chair of Catalysis Laboratory in NIFHI named after L.Ya. Karpov) to be heading this Department. Namely he possesses a merit of definition of a profile helping to train engineers on this specialty. To teach special courses at the Department and to supervise scientific work G.K. Boreskov involved the remarkable specialists in different questions of special technologies, such as I.V. Petryanov, M.G. Slin'ko, M.P. Malkov, L.M. Yakimenko. Already in the spring of 1950 the Department let out the first engineers – physical chemists who at once joined to solve real practical problems of nuclear branch. It is enough to mention R.A. Buyanov who during the period from 1950 to 1957 played one of the major roles in construction and startup of very difficult production of heavy water by a method of hydrogen low-temperature rectification in Chirchik. For this work R.A. Buyanov and M.G. Slin'ko have got the rank of Winners of the Lenin Award in 1960. G.K. Boreskov managed the Department up to 1960, having created during this time together with his disciples the new scientific direction "Isotopes in Catalysis". It is included both the use of isotope methods at research of catalysts and creation of catalysts for technology of stable isotope separation. After moving G.K. Boreskov to Novosibirsk many his disciples, graduates of the Department (V.V. Popovsky, V.S. Muzykantov, V.D. Sokolovsky) joined him. R.A. Buyanov and M.G. Slin'ko became deputy directors of Institute of Catalysis. After G.K. departure the catalytic direction of scientific works at the Department was continued by his disciples, and then by the disciples of their disciples. Today it is possible to note a number of significant results that are reached by the staff of the Department. Wide international popularity (France, Canada, Germany, England, and China) was gained by the hydrophobic platinum catalyst RCTU-3SM intended for separation of hydrogen isotopes by a method of chemical isotope exchange of hydrogen and water. Large amount of catalytic works directed on decontamination of the gas flows from tritium is carried out under contracts with the thermonuclear centers: Culham (Great Britain) and IO ITER (Kadarache, France). Fundamental studies of nanodimensional effects in catalysis of hydrogen homomolecular isotope exchange and *ortho*-*para*-conversion reactions with use of the rare-earth and noble metals are carried out under the leadership of G.K. Boreskov's disciple Dr. Sci. Chem. K.N. Zhavoronkova and her disciple PhD Chem. O.A. Boeva. Thus, the foundation laid under the Department by G.K. Boreskov was durable. With its help still many generations of students will gain knowledge in remarkable science under the name "catalysis".

ORAL PRESENTATIONS

Catalysts with single-atom sites of Pt-group metals for hydrogen production from decomposition of formic acid

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Supported Pt-group metals are well known catalysts for decomposition of biomass-derived formic acid giving H_2 for different applications. Recent studies showed that these catalysts may contain a significant ratio of single metal atoms, which can be very active in various reactions. For the first time, we have shown that deposition of 1 wt % of Pt-group metals (Pt, Pd, Ru) on different graphite-like *N-doped carbon materials* leads to creation of single-atom active sites for the formic acid decomposition [1-5]. In Pt catalysts, these sites provide stable and by more than 1 order of magnitude higher activity than the activity of metal atoms on the surface of nanoparticles supported on the N-free carbon or on the surface of unsupported Pt powder. Moreover, the conversion of formic acid on these sites gives only H_2 and CO_2 formation. In contrast to the N-doped catalysts, the N-free catalysts are more active in the reactions demanding surface metallic sites in nanoparticles like CO chemisorption and C_2H_4 hydrogenation by H_2. An atomic resolution HAADF/STEM study directly showed the presence of single atoms in the N-doped catalysts. Application of photoelectron spectroscopy based on synchrotron radiation for the *ex situ* reduced samples demonstrated that the single metal sites represent electron-deficient species interacting with pyridinic type nitrogen of the support. DFT calculations allowed concluding that a single metal atom may break the C-H bond in the formic acid molecule forming an adsorbed hydrogen atom and a carboxyl fragment only if this metal atom is attached to a pair of pyridinic N atoms in armchair configuration located on the graphene edge. We believe that catalysis with single atoms has bright future for further studies and applications.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 16-13-00016.

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OP-2

Effect of metal content in Au/TiO_2 catalysts for oxidation of n-octanol

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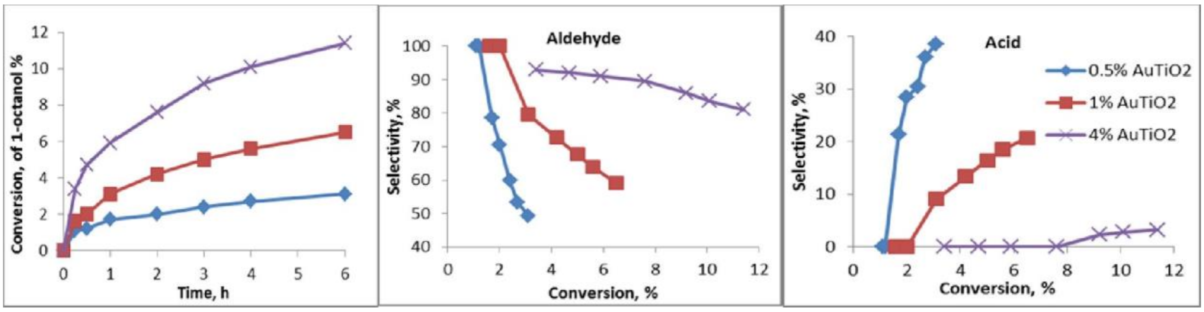
Nanosized gold based catalysts are among the most investigated systems for the aerobic green oxidation of alcohols, due to the surprisingly high activity of gold nanoparticles (Au NPs), but their activity for oxidation of long chain alkanols (fatty alcohols) have been less explored [1]. We have reported that Au/TiO_2 catalysts are effective for selective liquid phase oxidation of *n*-octanol as a model molecule for fatty alcohols [2]. Here we investigate influence of Au content in their performance (activity and selectivity) for this reaction.

Gold (nominal loadings: 0.5, 1 and 4 wt % Au) was supported on TiO_2 (Degussa P25, BET area 55 m^2g^{-1}) from aqueous solutions of $HAuCl_4 \times 3H_2O$ by deposition-precipitation (DP) with urea followed by vacuum drying at 80 °C for 2 h. Samples were characterized by UVvis, BET, XRD, HRTEM, XPS and FTIR of CO adsorption. Tests of *n*-octanol oxidation were made at 80 °C and atmospheric pressure for 6 h, using 0.1 M *n*-octanol in *n*-heptane with no base added, molar ratio *n*-octanol/metal = 100, and 30 mL/min O_2, and catalyst samples pretreated in H_2 flow at 300 °C for 1h. Reactants and products were analyzed by GC.

Catalytic activity increased with Au content (fig. left), though not proportionally however, the main effect occurs on selectivity. The trend to form acid (left) from octanal (center) decreases with the increase of Au content, while ester selectivity is not affected at low Au content. These results involve a tool to direct selectivity and will be discussed in terms of catalyst characteristics and the reaction mechanism.



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Theoretical insight into catalytic properties of ligand-protected gold clusters

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Gold nanoclusters protected by organic ligands, $[Au_nX_m]^q$, have crucial interest in homogeneous and heterogeneous catalysis including CO oxidation [1,2]. The application of $[Au_nX_m]^q$ as a catalysts has sufficient advantage, due to any property such as activity, selectivity or stability can correlate with particular composition and structure which are precisely defined. The mechanisms of catalytic reactions involving the $[Au_nX_m]^q$ are still to be clarified, the quantum chemical study of their properties at the atomic level seems to have great prospects.

Here we present the analysis of structure, electronic and chemical properties of $Au_{20}(SR)_{16}$ (R=CH_3, Ph) and $[Au_4(dpmp)_2X_2]^{2+}$ (X= –C≡CH, –C≡CCH_3, –CH_3, –SCH_3, –Cl; *dpmp* – bis(diphenylphosphinomethyl)phenylphosphine)); CO oxidation catalysed by the clusters and their fragments ($Au_2(SR)_3^-$, $(AuSR)_4$, $Au(AuSR)_4$, PPh_3AuCH_3) is also simulated to predict the active site and the mechanism of catalytic reactions involving $[Au_nX_m]^q$. Spin–polarized DFT/PBE level in the scalar–relativistic approach were used. The method has been tested in details in respect to predict structure and electronic properties of $[Au_nX_m]^q$.

According to calculation of $[Au_4(dpmp)_2X_2]^{2+}$ structure, it has flat Au_4 fragment stabilized by two opposite located X groups and two staple-like *dpmp*. The calculated Au–Au, Au–X, and Au–P distances agree with X ray data. The X ligand affects on the electronic cluster's stability, decomposition, and ligand exchange ability. The different pathways of CO oxidation on $[Au_4(dpmp)_2(C{\equiv}CCH_3)_2]^{2+}$ including ligand shell conserving or ligand exchange through breaking of one Au–P contact have been simulated. The calculated activation energies of all steps are small and suggest that the reaction can occurs at room temperatures.

The five isomers of $Au_{20}(SR)_{16}$ (R=CH_3, Ph) have been calculated. The Au_7 core consists of two tetrahedrons united by a common vertex; it is protected by an octameric ring, one triple and two monomeric staple motifs $SR(AuSR)_x$. The cluster can catalyzed CO oxidation, but the activation energies of the corresponding steps calculated for the fragments: $Au_2(SR)_3^-$, $(AuSR)_4$, $Au(AuSR)_4$, PPh_3AuCH_3 are less than for the clusters. This suggests that the atomic fragments of the ligand-protected gold clusters can be involved in catalysis.

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OP-4

Hydrogenation of CO_2 to Methanol: Influence of Polymorphic ZrO_2 Phases and Copper Electronic State on Activity of Cu/ZrO_2 Catalyst

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Methanol is considered a key material for C1 chemistry. It is produced on a large scale from synthesis gas with the use of heterogeneous catalysts. Carbon dioxide is also used in the feed. From the perspective of protection of natural environment, it would be highly desirable to replace CO by CO_2, as carbon dioxide is considered a greenhouse effect gas. Usually, copper catalyst on ZnO or ZrO_2 is used, supported on Cr_2O_3, Al_2O_3 or BeO to increase its thermal stability. Recently, it was observed that the Cu/ZrO_2 catalytic activity in CO_x hydrogenation depends on the polymorphic structure of zirconium oxide. Another factor which influences the catalytic activity of Cu/ZrO_2 systems, is the electronic state of copper phase. While amny attribute copper activity to positively charged copper ions, some argue that metallic copper is responsible for efficient hydrogenation of CO_2.

Our aim was to study i) the influence of the type of polymorphic ZrO_2 phase and ii) copper electronic state on the catalytic activity of Cu/ZrO_2 in hydrogenation of CO_2.

The Cu/ZrO_2 catalysts were obtained by co-precipitation and complexation, so that the t-ZrO_2/m-ZrO_2 ratio varied in the range 0-100 %. In addition to catalytic tests, investigations of the crystallographic structure by XRD method, studies of the catalysts surface structure by XPS and Auger, a reactive adsorption of N_2O, and the acidity measurements using pyridine adsorption were carried out. Quantum chemical calculations concerning oxygen vacancies with the participation of different crystallographic facets in both ZrO_2 polymorphs and on the influence of the electronic state of copper were done. It was found that variation of catalyst preparation conditions influences copper dispersion, its electronic state, and contents of the zirconia polymorphic phases [1]. The presence of oxygen vacancies stabilizes both the thermodynamically unstable t-ZrO_2 phase and Cu^+ cations. The catalytic activity toward methanol increases with increasing t-ZrO_2 content. Partial positive charge accumulated on copper greatly enhances interaction of the catalyst active phase with reactants [2].

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OP-5

A role of H_xMoO_3 (H_xWO_3) in the Pd catalysts in activity/selectivity control for hydrogenation of unsaturated aldehydes

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The effect of hydrogen-species existing in the matrix of hydrogen bronzes of MoO_3, WO_3 and H_2WO_4 – supported Pd catalysts (Pd 0.5-4 wt %) in controlling the selectivity to C=C/C=O hydrogenation (20-500 °C, 1-6 atm H_2, toluene) was studied for cinnamaldehyde (CAL) [1] and furfural (FU). In these molecules, the C=O bond is in the vicinity of C=C bond. CAL can serve as a model compound while FU is the key reagent obtained from renewable biomass. The impregnation of oxide supports (MoO_3, WO_3, H_2WO_4) with palladium acetate followed by hydrogen reduction (250 °C, 2 h) produced catalysts with Pd particles ca. 8-10 nm. The catalysts were characterized by XRD, XPS, SEM, TEM, HRTEM. To recognize a role of MoO_3/WO_3 – derived hydrogen bronzes the amount of hydrogen sorbed due to bronze formation together with thermal effects was determined by microcalorimetry. In the catalysts, the Pd particles were nearly monodispersed and well distributed at low Pd loading (0.5 % - 1 % Pd) but aggregated to some extent as the content of Pd increased. Hydrogen species in the bronzes have a beneficial effect on Pd crystallites formation. High mobility of hydrogen species in the bronzes structure assisted by migration of Pd ions facilitated by layered morphology of MoO_3 could promote the Pd crystallites of tetrahedral shape. This effect may also be responsible for specific location of Pd particles in the oxide matrix in form of a well organized structures consisting of parallel chains of Pd particles. The C=C group of CAL was preferentially hydrogenated compared to C=O group at low (0.5 % Pd) and high (4 % Pd) Pd content showing an effect of optimum Pd loading in the selectivity of CAL hydrogenation. The activity/selectivity behaviour of Pd/MoO_3 catalysts were related to hydrogen bronzes existing during the catalytic tests. The hydrogen-species generating effect was stronger for MoO_3 than for WO_3 supported catalysts. The presence of water molecules in the H_2WO_4 facilitated hydrogen induced activity/selectivity effects. Hydrogen bronzes of MoO_3, WO_3, H_2WO_4 provided additional active sites efficient for the activation of CAL/FU. It resulted in more active catalysts assisted by the promotion of C=C hydrogenation. Selectivity to saturated aldehyde in CAL hydrogenation attained ~95 %. In FU hydrogenation, the formation of tetrahydrofurfuryl alcohol was promoted at ~80 % selectivity. WO_3-based Pd catalysts exhibited low furan formation and almost stable activity.

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Propane oxidation over Pd/Al_2O_3 catalysts – the effect of palladium dispersion and C_3H_8:O_2 ratio on catalytic activity

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Lower alkanes (C_1-C_4) are now of great interest due to the opportunity of using them instead of gasoline or diesel as an energy source for automotive engines. However, in consequence of high values of magnitude of the greenhouse effect the complete afterburning of methane and its homologous is of high importance. Catalytic combustion of hydrocarbons is one of the most promising ways to restrain the greenhouse effect. Alumina supported palladium catalysts provide relatively high activity and stability in C_{2+} hydrocarbons oxidation. In this work, the catalytic properties of palladium-on-alumina catalysts in propane oxidation were studied. The influence of palladium particles size (3.5 nm, 4.5 nm, 7.5 nm), the reaction temperature (350, 400, 450 °C) and propane:oxygen ratio (1:1, 1:15) on the activity and stability of 1 % Pd/Al_2O_3 catalysts was revealed. XPS in situ experiments were conducted to obtain the information about the changes of palladium charge state at the surface of the catalyst under reaction conditions.

It was shown that in propane total oxidation reaction (C_3H_8 – 1 %, O_2 – 15 %, He as a balance) TOF values rises with palladium particles size. XPS in situ experiments revealed the almost linear correlation between the Pd^{2+}/Pd^0 ratio at the surface, palladium particles dispersion and TOF values.

For the rich mixture (C_3H_8 – 1 %, O_2 – 1 %, He as a balance) the dependence of the reaction pathway (total or partial oxidation of propane) on the reaction temperature and palladium dispersion was detected. Namely, the selectivity toward CO formation rises with palladium particles dispersion and strongly depends on the reaction temperature. At 350 °C only CO_2 and H_2O were detected, whereas at 450 °C carbon monooxide is the main reaction product. The CO concentration decreases with time and reaches the value of approx. 0.1 % vol. after 3 hours till the start of experiment for all the catalysts studied. According to the XPS ex situ data for fresh and aged samples, Pd^{2+}/Pd^0 ratio increases for the catalysts aged under reaction conditions.

Thus, it can be concluded that the ratio between metallic (Pd^0) and oxidized (Pd^{2+}) states of palladium on the surface of the catalyst is one of the key factors controlling its activity in propane total and partial oxidation reactions.

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OP-7

Boosting effect of Mo on activity and stability of Ni-based self-organizing catalyst

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Chlorinated hydrocarbons (CHCs) are known to be hazardous pollutants contained in various waste oils and other organic liquids. They constitute one of the most important classes of organic pollutants by virtue of their environmental impact and toxic effects. [1]. There is a wide range of methods suggested for CHCs processing among which the catalytic approaches are considered to be the most effective ones.

A catalytic decomposition of chlorinated hydrocarbons, including their complex mixtures and waste products, to obtain a nanostructured carbon material (CNM) attracts much attention today as a promising way of organochlorine waste disposal [2]. This method is based on catalytic action of so-called self-organizing Ni-based systems, resulting from the disintegration (metal dusting) of bulk Ni-M alloyed precursors under reaction conditions. It has previously been shown that a catalytic activity and stability of self-organizing Ni-M catalysts might be significantly influenced by the nature and concentration of metal M used as an alloying component for the synthesis of Ni-M precursors [3].

In the present research we have investigated regularities of carbon erosion process of micro-dispersed alloys $Ni_{1-x}Mo_x$ (x = 0÷10 %) synthesized by the co-precipitation of salts precursors followed by sintering in a reducing atmosphere. Formation of $Ni_{1-x}Mo_x$ alloys was controlled the XRD analysis. The effect of molybdenum on catalytic activity of self-organizing system $Ni_{1-x}Mo_x$ and its resistance to deactivation during the decomposition of 1,2-dichloroethane to yield CNM will be discussed. The most active sample containing 8 at.% of Mo was successfully tested in processing of real waste products (vinyl chloride production, Sayansk, Russia) into carbon nanomaterial.

A particular attention will be paid to the structural and morphologic peculiarities of carbon material resulted from the decomposition of 1,2-dichloroethane at $Ni_{1-x}Mo_x$ catalysts.

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OP-8

Formation of Active Sites over Pd/CeO_2 Catalysts for wet CO oxidation under ambient conditions

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The catalysts resistance to wet poisoning is a serious problem for their practical application for air purification from carbon monoxide under near-ambient conditions. In most cases the positive or negative effect of water on the catalytic performance of supported Pd catalysts in CO oxidation is strongly depended on the moisture content in the feed gas.

In the present work, the influence of humidity on catalytic performance of the two highly dispersed 1 % Pd/CeO_2 catalysts were performed at isothermal conditions at ambient temperature. CeO_2 supports were prepared by different methods described elsewhere [1-2] The formation and reactivity of surface sites and intermediates during CO oxidation was investigated by *in situ* FTIR and UV-Vis DR spectroscopy and TPR methods.

When the support was prepared by traditional precipitation [1], the Pd/CeO_2 catalyst demonstrated 80 % CO conversion under dry conditions. The addition of H_2O into the feed was found to decrease the activity. The initial Pd^{2+} sites of Pd/CeO_2 catalysts can be easily reduced by CO to form Pd^0 and $Pd^{\delta+}$, and reoxidized by O_2 to form $Pd^{2+(-\delta)}$ species. The FTIRS study showed that the positive or negative effect of moisture depends strongly on the water coverage of the surface. In humid atmospheres at a low water coverage (<20 %) the Pd^{2+} reduction and Pd^0 reoxidation was promoted. At a high water coverage (>50 %) the Pd^0 species were not reoxidatized even in O_2 excess. As a result the catalyst was deactivated. Pd^0 species was inactive for low-temperature CO oxidation. The active sites include the partially charged small metal clusters ($Pd^{\delta+}$) in the vicinity of the $Pd^{2+(-\delta)}$-OH groups.

The interaction of CO with weakly bonded oxygen of ceria resulted in formation carbonite, noncoordinated carbonate and bidentate carbonate surface species. The latter species reacted with specific Pd-OH groups forming bicarbonate, which can be easily decomposed to CO_2. In wet conditions new formate species accumulated at the catalyst surface. It seems the formates can block oxygen vacancies and terminate O_2 activation under excessive water coverage of the surface. This process resulted in a fast palladium reduction.

When the hydrophobic support prepared in the presence of polyvinyl alcohol (PVA) was used for catalyst synthesis [2], the better stabilization of the $Pd^{\delta+}$ - $Pd^{2+(-\delta)}$ active sites was observed in wet condition. The Pd/CeO_2-PVA catalyst demonstrated 90 % CO conversion at the initial reaction moment and 50 % at the steady-state conditions in the presence of H_2O.

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OP-9

The transformations of the copper-based co-catalysts of the $Cd_{0.3}Zn_{0.7}S$ photocatalyst at the hydrogen photoproduction under visible light

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Hydrogen as environmental friendly and high-energy fuel has attracted attention all over the world for the last decade. Photocatalytic water splitting under the visible light is a very promising and interesting method of the H_2 production. To achieve the higher efficiency for photocatalytic water splitting many researchers in this field involved electron donors as "sacrificial agents". One of the most commonly used sacrificial agents is Na_2S/Na_2SO_3 system. $Cd_{1-x}Zn_xS$ solid solution with a controllable bandgap width and band-edge position is an efficient photocatalyst for H_2 production from water solutions of Na_2S/Na_2SO_3 under visible light [1]. To improve the photocatalytic activity of $Cd_{1-x}Zn_xS$ solid solution, many modification approaches have been developed. In our previous work we have shown that CuS-doping increased the photocatalytic activity of $Cd_{0.3}Zn_{0.7}S$ [2].

In this research the promotion of activity of the $Cd_{0.3}Zn_{0.7}S$ system with various copper species, such as Cu_xS and Cu, as a co-catalyst, in the photocatalytic hydrogen production from aqueous solutions of Na_2S/Na_2SO_3 under visible light irradiation was studied. The samples were characterized with a wide range of techniques. Also, the transformation of the photocatalysts during the catalytic runs was studied using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The highest apparent quantum efficiency and photocatalytic activity achieved at 450 nm over the 0.1 wt % $Cu_xS/Cd_{0.3}Zn_{0.7}S$ sample for the photocatalytic hydrogen evolution from Na_2S/Na_2SO_3 aqueous solutions were 23.1 % and 6.4 mmol g^{-1} h^{-1}, respectively, these values are quite high for H_2 evolution over photocatalysts without noble metals [3]. It was shown that deposited copper sulfide species CuS/Cu_2S with a particle size of ca. 5 nm are formed *in situ* from both CuS nanoplates with a length of approximately 200 nm and metallic copper nanoparticles during the operation of photocatalysts in aqueous solutions of Na_2S/Na_2SO_3, and namely the copper sulfide nanoparticles increase the activity of the $Cd_{1-x}Zn_xS$ solid solutions, which agrees well with the principles established by G.K. Boreskov in the 1950s [4].

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OP-10

Chemoselective Reduction of Carvone to Dihydrocarvone Over Au Catalyst

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Selective transformation of multifunctional organic molecules is one of the main challenges in catalytic fine organics synthesis. Carvone is one of the most widespread natural monoterpenoids [1], which is widely used in food, perfumery industry, and in the synthesis of fine chemicals. Carvone hydrogenation results in a valuable compound-dihydrocarvone which is formed as a mixture of two stereoisomers with a spearmint-like odor used as a food flavoring additive. Carvone is an interesting substrate to explore catalytic activity in stereo- and chemoselective hydrogenation, since it contains an asymmetric center with a specific configuration as well as three types of functional groups, which can be hydrogenated: C=O, a conjugated C=C and an isolated C=C groups [2,3]. The current work focuses on carvone hydrogenation over a gold catalyst to investigate both activity in competitive hydrogenation of different functional groups and to develop a feasible approach of dihydrocarvone synthesis.

Hydrogenation of carvone (10 mmol) in an alcohol (36 mL) was carried over 2%Au/TiO_2 (336 mg) at 100 °C in H_2 (9 bar). The reaction products were analyzed by *Tzvet-500* using a Carbowax-20M column (50 m, 0.2 mm, 0.5 µm, FID 250 °C) at 160 °C. ^{1}H-NMR spectra were recorded by *Bruker AV-400* spectrometer (400.13 MHz (^{1}H)) in the $CDCl_3$.

Au/TiO_2 catalyst has demonstrated high activity as well as stereo- and chemoselectivity in conjugated C=C double bond hydrogenation with predominant formation of *trans*-dihydrocarvone. The catalytic activity and *trans*- to *cis*- isomers ratio were shown to strongly depend on the solvent. Catalytic activity and *trans*- to *cis*-dihydrocarvone ratio increased in the following: 2-propanol < ethanol < methanol. The highest total selectivity to dihydrocarvone 62 % was achieved at a nearly complete carvone conversion (90 %) after 13 h in the case of methanol, with the *trans*-to-*cis*-dihydrocarvone ratio being about 1.8. Based on the transition state theory a quantitative description of *trans*- to *cis*-dihydrocarvone ratio variations in different solvents was made [4].

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OP-11

Mechanistic studies of reactions on nanosized catalysts with the use of parahydrogen

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Mechanistic studies are highly important for development of more active and selective catalysts for various industrially important catalytic processes. One of the most useful techniques for investigation of reactions involving hydrogen is parahydrogen-induced polarization (PHIP). Utilization of parahydrogen in hydrogenation reactions enables significant enhancement of NMR signals of reaction products and/or intermediates in case if two atoms of parahydrogen molecule are added to a substrate molecule as a pair. Thus, PHIP allows one to rule out the possibility of pairwise hydrogen addition and to detect minor reaction products or short-lived intermediates.

Herein, PHIP technique was applied for mechanistic studies of heterogeneous gas phase hydrogenation of various six-membered cyclic hydrocarbons over Rh, Pd and Pt nanoparticles supported on TiO_2 [1]. Hydrogenation of 1,3-cyclohexadiene and 1,4-cyclohexadiene with parahydrogen demonstrated the possibility of migration of C=C bonds in 1,4-cyclohexadiene and cyclohexene. In hydrogenation of cyclohexene the PHIP effects on reactant’s NMR signals were observed. Spectral simulations proved that the reason of this pairwise replacement effect is cyclohexene dehydrogenation to 1,3-cyclohexadiene and its subsequent pairwise hydrogenation to cyclohexene. In hydrogenation of benzene and toluene PHIP effects were not observed, implying either difference in the reaction mechanism compared to cyclohexene and cyclohexadienes hydrogenations or unimpeded migration of H atoms on the catalyst surface in case of arenes due to lower coverage of surface with an adsorbed substrate.

Also mechanistic insight into the semihydrogenation of 1-butyne and 2-butyne on Cu nanoparticles supported on partially dehydroxylated silica (Cu/SiO_{2-700}) was obtained using parahydrogen [2]. It was found that the surface modification of this catalyst with tricyclohexylphosphine (PCy_3) increases the selectivity in hydrogenation of butynes to butenes up to nearly 100 %, although at the expense of a reduced catalytic activity. For the first time, PHIP effects were observed in hydrogenation reactions catalyzed by Cu-based catalysts. Contribution of pairwise hydrogen addition to 1-butyne was estimated as at least 0.2-0.6 % for unmodified Cu/SiO_{2-700} and ≥ 2.7 % for Cu/SiO_{2-700} modified with PCy_3, highlighting the effect of the Cu surface modification with the tricyclohexylphosphine ligand.

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OP-12

Insights into the mechanism of H_2O_2-based epoxidations over Nb-containing catalysts

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Mesoporous niobium-silicates prepared by different methodologies are efficient catalysts for epoxidation of both electron-rich and electron-deficient C=C bonds with H_2O_2 as green oxidant [1,2]. Here we provide new insights into the mechanism of the H_2O_2-based epoxidations from reaction kinetics analysis and spectroscopic studies using two types of Nb-catalysts, viz. mesoporous niobium-silicates prepared by evaporation-induced self-assembly (EISA) and soluble Nb-containing polyoxometalate (Nb-POM). Two types of model substrates, cyclooctene (CyO) and 2-methyl-1,4-naphthoquinone (MNQ), were employed to understand peculiarities of epoxidation of electron-rich and electron-deficient C=C bonds.

The EISA methodology enables preparation of hydrothermally stable mesoporous niobium-silicates with easy control of the state of Nb active centres through a proper choice of the Nb precursor [2]. The observed kinetic regularities did not depend on the state of the Nb centres (isolated or oligomeric) but were determined by the nature of organic substrate, indicating different oxidation pathways for epoxidation of electron-rich (CyO) and electron-deficient (MNQ) C=C bonds. The rate low found for CyO is consistent with a mechanism that involves interaction of H_2O_2 with Nb(V) to give a hydroperoxocomplex 'NbOOH' and water followed by subsequent electrophilic oxygen transfer from 'NbOOH' to C=C bond, producing epoxide and regenerating the initial state of the catalyst. In the case of MNQ, the observed kinetic regularities allowed us to suggest a more complicated mechanism that involves the formation of 'NbOOH', oxidation of the solvent molecule (MeCN) to form peroxycarboximidic acid $H_3CC(=NH)OOH$ that reacts fast with electron-deficient C=C bond, producing epoxy derivative and acetamide (the so-called Payne oxidation). This hypothesis was further supported by a rate-accelerating effect of base (typical of Payne oxidation), lack of the reaction in ethylacetate, and accumulation of acetamide during the reaction.

Comparative study of the catalytic performances of mesoporous niobium-silicates and Nb-POM showed that POM of the Lindqvist structure, $(Bu_4N)_3NbW_5O_{19}$, mimics well the catalytic action of niobium-silicates and can serve as a tractable molecular model to get further insights into the structure and reactivity of Nb(V) peroxo species using various spectroscopic techniques (UV-vis, ^{93}Nb and ^{183}W NMR and others).

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Simple and complex metal oxide catalysts of red-ox reactions: bonding strength of surface oxygen species, their mobility and reactivity

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Among the concepts developed by G.K. Boreskov for oxidation catalysis, the bonding strength of surface oxygen species as a measure of their reactivity determining catalytic properties of oxide catalysts plays a central role [1]. Here results of research aimed at further development of this concept for main types of oxide catalysts with a due regard for their real bulk/surface structure and composition affecting the nature of sites [2-6] are reviewed. Simple transition metal oxides (CuO, Fe_2O_3, Cr_2O_3, NiO, etc) were prepared by decomposition of nitrate salts or hydroxides, while complex oxides with spinel, perovskites, fluorite structures were prepared by modified Pechini route. Real structure was studied by XRD, TEM, Raman, FTIRS of lattice modes, surface properties – by XPS, SIMS, FTIRS of adsorbed CO/NO. Bonding strength of surface oxygen species, their coverage, mobility and reactivity were characterized by O_2 TPD, pulse microcalorimetry, TAP, oxygen isotope heteroexchange with $^{18}O_2$ and $C^{18}O_2$ in isothermal, temperature-programmed and SSITKA modes. Theoretical estimation of the heats of oxygen adsorption for different types of surface sites was carried out by semi-empirical Interacting Bonds Method. Catalytic properties of pure oxides were estimated in the reactions of CO oxidation and combustion of hydrocarbons, while those with supported Ni and/or Pt group metals – in fuels reforming into syngas.

Weakly bound terminal MO surface oxygen forms (Q_{ads} in the range of 40-400 kJ/mol) determine specific activity in deep oxidation reactions. They are mainly located at scarcely developed rough surface faces or associated with surface defects/outlets of extended defects, so for the same oxide phase their coverage broadly varies depending upon the real/defect structure of sample and its stoichiometry. Bridging M_2O surface oxygen forms (Q_{ads} up to 700 kJ/mol) determine activity of metal-promoted oxides in reducing conditions of fuels reforming. They are located at regular sites of the most developed densely packed faces migrating to Me-support interface by the surface/near surface diffusion and transforming activated on Me sites C-H-O species into syngas.

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OP-14

The Mechanism of the lower Alkenes Epoxidation by α-Oxygen on the FeZSM-5 Surface

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It is known that the ethylene epoxidation proceeds with high selectivity on Ag catalyst. The reaction is assumed to occurs via participation of the electrophilic type of oxygen, $O_{elect.}$. However, in the case of propylene this oxygen, instead of the C = C bonds, preferably attacks the weakly bounded allylic hydrogen, resulting in a low selectivity to propylene oxide.

A convenient model of O_{elect} is the anion radical $O^{\bullet-}$, which is as a part of the activated α-site $(Fe^{III}{-}O^{\bullet-})_\alpha$ on FeZSM-5 zeolite [1]. α-Oxygen exhibits a very high reactivity. The stoichiometric surface oxidation of methane (titration) $CH_4 + (Fe^{III}{-}O^{\bullet-})_\alpha$ can proceed by the hydrogen abstraction mechanism even at –60 °C leading to hydroxo-complexes $(Fe^{III}{-}OH)_\alpha$, which can be reliably registered by FTIR (Fig. 1a, bands 3675 and 3630 см$^{-1}$).

To verify the mechanistic role of allylic hydrogen we performed a comparative study of the ethylene and propylene oxidation by α-oxygen at 25 and –60 °C [2]. If in the case of propylene α-oxygen really attacks the allylic C-H bond this should lead to a spectrum, which is similar to that of methane. However, it is not the case (Fig. 1b). Oxidation of both alkenes leads to the spectra with no signs of $(Fe^{III}{-}OH)_\alpha$ complexes. The subsequent extraction of the formed surface compounds showed that in both cases the epoxides were the only primary products partially subjected to some secondary transformations. A similar result was obtained with 1-butene.

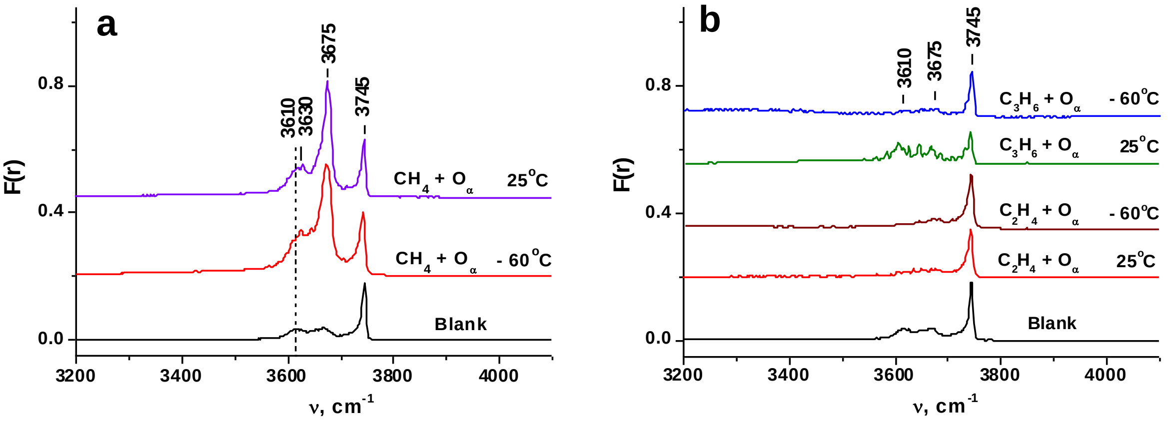

Fig. 1. FTIR spectra after α-oxygen reaction with methane (a), ethylene and propylene (b)

The obtained results show the need for additional research of the mechanistic role of allylic hydrogen. Based on DFT calculations a reaction mechanism via the intermediate formation of ferraoxetane cycle was proposed.

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OP-15

Reactivity and transfer kinetics of surface and subsurface oxygen species in CO oxidation on Pd(110)

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Thermodesorption spectroscopy and temperature-programmed reaction using a beam-forming gas doser and oxygen isotopes $^{18}O_2$ and $^{16}O_2$ have been applied for studying the titration of adsorbed O_{ads} and subsurface oxygen O_{subs} on a reconstructed Pd(110) surface. Subsurface oxygen appears to be non-reactive. However, as the reaction proceeds, it comes onto the surface and interacts with adsorbed CO. Numerical simulations have been applied to investigate the $O_{subs} \rightarrow O_{ads}$ transfer kinetics. On the reconstructed surface the stage $O_{subs} \rightarrow O_{ads}$ is reversible, and its rate is linearly dependent on the concentration of surface sites freed during the reaction $O_{ads} + CO_{ads} \rightarrow CO_2$. The temperature dependencies of direct and reversed reaction rate constants have been determined. As the adsorbed oxygen concentration decreases to some threshold value, a self-accelerated irreversible subsurface oxygen outcome occurs caused by a surface reconstruction to the structure (1×1). The kinetic equation for the process has been suggested. The temperature dependence of the critical surface oxygen coverage initiating the surface reverse reconstruction has been determined [1].

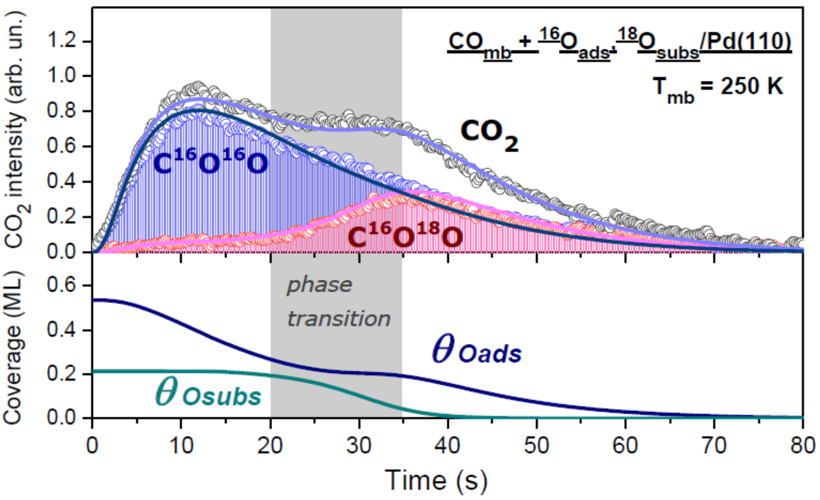

Fig. 1. Experimental and calculated CO_2, $C^{16}O^{16}O$ and $C^{16}O^{18}O$ formation rates, θ_{Oads} and θ_{Osubs} during the $C^{16}O$ supply onto the preliminarily adsorbed layer (0.2 L $^{18}O_2$ + 0.8 L $^{16}O_2$) at $T_{mb} = 250$ K

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0001 for Boreskov Institute of Catalysis SB RAS.

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OP-16

Thermal Hysteresis in Methane Oxidation Properties of Pt,Pd-doped Mn-hexaaluminate Catalyst: Effect of calcination Temperature and Pt/Pd Ratio

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The Pd-modified Mn-alumina catalysts are known to be perspective for the catalytic combustion chamber of small gas turbines [1-3]. We have discussed a non-additive increase of their catalytic activity in the high-temperature oxidation of methane compared with Mn-alumina and Pd-alumina catalysts [4, 5]. Characterization of fresh catalysts by TPR-H_2, XRD and HRTEM has shown that their initial oxidative activity is associated with 2-5 nm sized PdO particles, having intimate contacts with particles of metallic Pd (100-300 nm) and imperfect Mn-hexaaluminate [5].

Here TPR-CH_4, TPR-O_2, in situ XRD and ex situ HRTEM were used to identify a role of the nanoscale state of noble metals and manganese cations in the high-temperature methane oxidation activity of the Pd,Pt-doped Mn-hexaaluminate catalysts. Calcination temperature and Pt/Pd ratio were found to have great influence on the catalytic behavior and thermal hysteresis. The positive effect on the methane oxidation activity was shown to be indeed due to the high-dispersed PdO nanoparticles located on the surface of metallic Pd particles. The PdO transformation to metal at 690-715 °C was reversible under the reaction conditions. There is PdO reformation at 570-590 °C. Mn^{3+} cations in the spinel blocks of Mn-hexaaluminate promote the PdO reformation. The temperatures of PdO transformation and reformation varied depending on O_2/CH_4 ratio of reaction feed. A decrease of the share of PdO nanoparticles due to both a increase of Pt loading in the catalyst above Pt/Pd = 0.3 and a high-temperature sintering of Pd metal particles under the reaction conditions result in lowering of the catalytic activity of Pt,Pd-doped $MnLaAl_{11}O_{19}$ catalysts. PtPd-alloy that was observed by TPR-H_2, HRTEM, and XRD in the catalyst with Pt/Pd > 0.3 ensure the high-temperature methane oxidation at 800-850 °C, although PtPd-alloy possess the lower methane oxidation activity compared with PdO and PdO_x/Pd.

Therefore, the design of effective catalysts was found to include the optimum content of the catalytically active PdO nanoparticles located on particles of metallic Pd and PtPd alloy.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (grant 15-03-05459-a).

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OP-17

Design and Synthesis of Nanocatalysts for Industrial Applications

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It is an ongoing scientific challenge to meet stringent sulfur levels of emissions from industrial sources. Sulfur emissions may contain oxidized sulfur, such as SO_2 and SO_3 or reduced sulfur, H_2S. Desulfurization is also needed to purify a gas stream for further utilization as a chemical feedstock. We have designed a class of mixed metal oxide compositions, derived from hydrotalcite-type clays, which can be used for effective abatement of oxidized and reduced sulfur. The primary factors for the effectiveness of these materials are compositions, nano-range crystallites, redox metals, and unique structural domains. To be effective these materials need to have three functions: 1) chemisorption and transfer of "sulfur" from gas to solid, 2) retention of catalytic properties of the solid to perform other gas phase catalytic reactions, such as the water gas shift reaction, and 3) effective release of the sulfur for the regeneration of the catalyst. This paper will discuss how these three functions were studied and enhanced by designing novel mixed metal oxide materials for effective desulfurization of hot gases from gasification units and refineries.

Acknowledgement. This work was supported by Honeywell UOP

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Oxidative catalysis processes in the biorefinery of wood biomass

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The huge resources of lignocellulosic biomass are presented by wood which can be used as an important renewable feedstock for production of valuable chemicals and biofuels. The advanced biorefinery should integrate the processes of biomass transformation that are optimized for energy efficiency and resource utilization. The promising approaches in the development of high-tech processes of lignocellulosic biomass conversion into valuable chemicals and biofuels are based on the fractionation of its main components – polysaccharides and lignin. Oxidative catalytic fractionation of biomass can be considered as a key stage of wood biorefinery.

This presentation described the green processes of catalytic fractionation of hard- and softwoods by H_2O_2 and O_2 on cellulose and soluble products from lignin and hemicelluloses.

Air dry sawdust of aspen, birch, abies and pine wood were used. Catalytic processes of wood oxidation were studied with the use of stirring fixed-bed reactors. FTIR, XRD, SEM and chemical methods were used for study the solid products. Low molecular mass products were identified by GC, HPLC and GC-MC methods.

Suspended TiO_2 catalyst was successfully used for wood peroxide fractionation on microcrystalline cellulose and soluble products at mild conditions (100 °C, atmospheric pressure) in the acetic acid – water medium. For all type of wood the processes are described by the first order equations and have the activation energies 76-86 kJ/mol. The optimized conditions of wood fractionation processes were established by experimental and mathematical methods.

Aerobic catalytic oxidation of wood lignin to aromatic aldehydes was accomplished in water-alkaline medium in the presence of suspended $Cu(OH)_2$. This catalyst intensifies the oxidation of wood lignin by O_2 to aromatic aldehydes at 150-160 °C. At optimum conditions the total yield of vanillin and syringaldehyde reaches to 43 % mas. relative to hardwood lignin. Aerobic oxidation of softwood lignin gives mainly vanillin with the yield to 18 % mas.

The new approach to catalytic biorefinery of wood was developed which based on wood oxidative catalytic fractionation on cellulose and soluble products from lignin and hemicelluloses. The developed catalytic biorefinery of wood makes it possible to achive the utilization of all main components of woody biomass by environmentally friendly way.

Acknowledgements. The reported study was supported by the Russian Science Foundation (Grant N 16-13-10326). This work is part of GDRI "Catalytic biomass transformation" between France and Russia.

Catalytic oxidation of CO on CuO_x: specificity of the reaction medium effect on the kinetics due to a partial flexibility of the surface structure

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Among basic concepts of oxidation heterogeneous catalysis developed by G.K.Boreskov, effect of reaction media on the state of catalyst, and, hence, on observed kinetic parameters takes one of the central place [1, 2]. It was described by the linear dependence of the activation energy of rate-limiting stage on the oxygen bonding strength being a function of the surface oxygen coverage varied with temperature or O_2/reagent ratio in the feed. Further development of this concept requires to take into account rearrangement of the surface layer due to variation of its oxygen stoichiometry.

For mechanism of CO catalytic oxidation by oxygen on CuO, analysis of kinetic features of CuO_x reduction by CO pulses combined with monitoring the state of the surface by an electrochemical technique using a solid electrolyte-Pyrex glass, FTIR spectroscopy of adsorbed CO and high resolution TEM data on the defect structure of CuO allowed to suggest a partially ‘‘flexible’’ model of CuO surface [3-6]. This model assigns the most active surface sites able to coordinate highly reactive CO and O terminal forms to clusters of Cu+ cations located at outlets of extended defects (dislocations, twins). Their density increases with the surface reduction, thus counteracting the negative effect of the increase of the average oxygen bonding strength on CuO activity/reactivity. A fast lattice oxygen diffusion along these extended defects was revealed as well. Variation of the number, size and structure of these clusters under the reaction medium effect allows explaining the difference between the quasi-steady and true steady states of copper oxides in catalytic CO oxidation reaction as well as the difference between kinetic parameters of reaction estimated at quasi-steady and constant states of the surface following Boreskov’s approach. For clustered defect centers of CuO, reaction kinetics corresponds to the Langmuir-Hinshelwood mechanism. For the true steady-state corresponding for all phases in Cu-O system to disordered defect cuprite-type $Cu_{2-\gamma}O_{1+\delta}$ phase, destruction of extended defects due to prolonged action of reaction media at high temperatures results in a low activity due to absence of such clustered active centers.

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OP-20

The way to control the reactivity of Cu-nanoparticles in the oxide catalysts of C_1-molecules reactions

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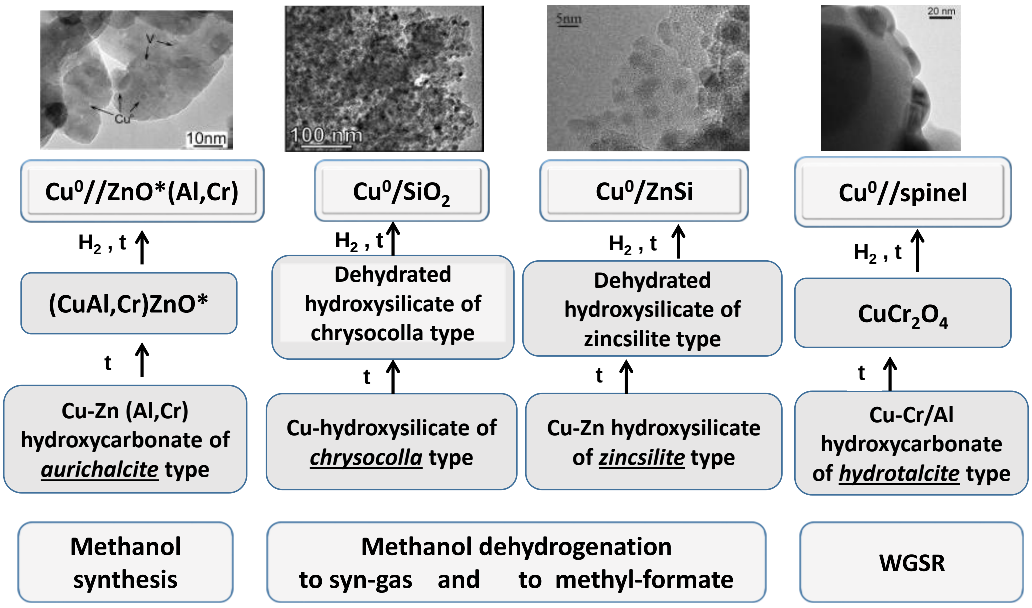
Active in hydrogenation reactions Cu-containing oxide catalyst are commonly produced via thermal decomposition of hydroxycarbonates and hydroxysilicates at certain temperature following by reductive activation with H_2. For elucidating the possibility to control the composition and the method to produce highly effective catalysts, the structural transformations and catalytic behavior in syn-gas reactions of Cu-Zn/Al/Cr/Si oxides (different ratio) have been studied. Cu-nanoparticles formed upon activation determine the catalytic properties and their properties depend on the nature of interaction with supporting oxide (ZnO, SiO_2, spinel, Zn-hydroxosilicate). Analysis of our data and published results allows concluding that there are three possible types of Cu-nanoparticles interaction with oxide supports: (1) epitaxial bonding to the surface of supporting oxide; (2) decorating with clusters of supporting oxide (ZnO_x AlO_x SiO_x); and (3) combination of (1) and (2). The Scheme below illustrates the way to provide high efficiency of Cu-nanoparticles [1-5]:



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OP-21

Current Status of Research and Development Prospects of the Process and Catalysts of Gasoline Fractions Reforming

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The problems associated with the currently existing trends of the need to increase the efficiency of modern refining naptha processes (reforming, isomerization) at simultaneous tightening of the requirements for environmental safety of fuel are discussed.

Studies of the structure of the active centers of catalysts of reforming, biforming, isomerization of C_5-C_6 alkanes, hydroisomerization of arenes and hydrocracking of C_7 alkanes that are developing in IHCP SB RAS formed the basis of a systematic approach to their preparation, which allowed to solve the complex issues of increasing the efficiency of their actions for activity, selectivity and resistance to deactivation in work and regeneration cycles for a fairly short time [1]. The experience of solving of the problems in the process of development of new industrial catalysts is analyzed.

The prospects of using integrated naphtha refining processes with a combination of previously known processes (reforming, isomerization) and new processes (biforming, ekoforming) with the inclusion of benzene-methylcyclopentane isomerisation and n-alkanes selective cracking steps in its technological schemes are substantiated.

The usage of such schemes allows to product fuels Class 4 and 5 without using of oxygenates and other expensive fuel additives.

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OP-22

Nonlinear Phenomena in Heterogeneous Catalytic Systems

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The reactions of CO oxidation over Pt and Rh and methane oxidation over Pd will be discussed. It will be shown how the nonlinear mechanism of these reactions can change the way in which usually heterogeneous reactions proceed. Firstly it will be shown that the kinetic oscillations and synergetic effect can originate due to the diffusion coupling of two different catalysts, where the CO oxidation proceeds in a steady state regime. Secondly it will be demonstrated that due to the nonlinearity of the system and the ability to form spatial structures the two Pd catalysts can produce the same catalytic activity as one Pd catalyst during methane oxidation.

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OP-23

Simplest mechanism of self-sustained oscillations in the partial oxidation of methane over Ni

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Under conditions of heterogeneous catalytic reaction there could be observed the oscillating changes of concentrations of the reaction products even if concentrations of the reagents in the reactor inlet are constant. Such dynamics could be caused, for example, by periodical changes of the catalyst surface properties.

We experimentally studied the dynamics of oxidation of methane over Ni foil [1]. For some gas temperatures as well as the methane and oxygen partial pressures at the reactor inlet we observed self-sustained oscillations of concentrations of the reaction reagents and products (CO, H_2, CO_2, and H_2O). These oscillations are accompanied by periodical changes of the catalyst temperature. Using SEM we showed that the catalyst structure changed sufficiently under the reaction conditions, which is caused by reversible oxidation of metallic Ni to NiO [1].

Developing kinetic model we, firstly, considered reaction mechanism, which includes dissociative adsorption of methane and oxygen on Ni. While CO, H_2, CO_2, and H_2O are considered as products of reactions on the catalyst surface and subsequent desorption of corresponding surface species [2].

Moreover, experimentally we observed that selectivity of the reaction according to CO and H_2 is enough large. Thus using the quasi-steady-state approximation we proposed the simplest 5-steps mechanism of partial oxidation of methane over Ni. We developed a kinetic model, according to the mechanism, and a model of CSTR reactor. Our simulations showed that the model could well describe some experimentally observed relaxation self-sustained oscillations of methane, oxygen, CO and H_2.

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0003 for Boreskov Institute of Catalysis.

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OP-24

Boreskov concept about the influence of the reaction medium on the catalyst. Example of CO oxidation reaction

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One of the basic approaches in the description of such a complex phenomenon as catalysis is the concept of the reaction medium impact on the catalyst that was proposed by G.K. Boreskov in the 70s of the 20th century. According to this concept, the reaction medium and the catalyst are considered as an ensemble mutually responding to external conditions and thus determining the catalytic activity. Basically, the concept of Boreskov is in line with known modern concepts of "pressure gap" and "material gap", which consider catalytic system from the low pressures with the realization of simple mechanisms to high pressures with complex composition and structure of the catalysts and consideration of complex mechanisms.

For oxidation reactions on metals the influence of the reaction medium mainly leads to surface oxidation with formation of different surface oxide phases, and at higher pressures of reagents results in deeper oxidation and formation of a thermodynamically stable and metastable oxide phases.

In this paper on the example of the model reaction of carbon monoxide oxidation on platinum group metals (Pd, Pt, Ir) the kinetic aspects of this reaction in full pressure range are considered depending on composition and structure of the catalysts. Effect of structure is considered starting from the simple systems: single crystals and polycrystalline samples and then moving to the nanostructured supported systems and complex composite systems with a maximum dispersion of metals up to the ionic state. The use of ultra-high vacuum conditions and single crystal samples allowed establishing the elementary stages and the basic mechanism of the oxidation reaction. The increase of the reactants pressure led to the observation of self-oscillations and hysteresis of the reaction rates. These phenomena were explained by the catalytic oxidation-reduction of metal surfaces, particularly with formation of so-called "subsurface" oxygen species or "surface oxide". As a rule, hysteresis phenomena could be characterized by a "normal" behavior with varying of the temperature while the self-oscillations might be of different kinds. Transition to "torr-range" pressure of the reaction medium and supported metallic systems was characterized by structural transformations of bulk metal/metal oxide and the formation of "core-shell" structures with kinetic peculiarities in the form of the reverse temperature hysteresis and high-amplitude relaxations in self-oscillations of the reaction rate.

In this work some approaches for description of kinetic behavior and mechanisms of the reaction are also discussed.

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OP-25

$Pt_{0.5}M_{0.5}$ and Pt-MO_x (M = Fe, Ni, Co) model catalysts in total and preferential CO oxidation

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The use of supported alloy nanoparticles is a promising way to modify activity and selectivity, improve stability or at least partially substitute expensive noble metals in conventional supported metallic catalysts, such as Pt-, Pd- and Rh-based systems. One of the reactions in which the properties of conventional Pt-based catalysts are needed to be improved is CO preferential oxidation (CO PROX) − a case of substrate-selective oxidation of CO in a huge excess of H_2. The CO PROX is considered as a promising way for deep CO removal from hydrogen-rich gas mixtures for proton-exchange membrane fuel cells (PEMFCs) feeding. A number of Pt-M (M = Co, Ni, Cu, etc.) bimetallic systems showed a remarkable synergetic effect in CO PROX compared to Pt. However it is yet unclear whether the electronic effect of Pt-M interaction (“ligand effect”) or Pt-MO_x interface (“ensemble effect”) causes the synergism. In order to distinguish it, we have synthesized and studied the CO PROX performance of the unsupported model catalysts with $Pt_{0.5}M_{0.5}$ (M = Fe, Co, Ni) solid solution and Pt-MO_x metal-oxide composite structures.

The addition of second metal dramatically enhanced the activity of Pt towards CO oxidation (Fig. 1) providing high activity at near-ambient temperatures in both total and preferential CO oxidation. The synergetic effect was pronounced for both $Pt_{0.5}M_{0.5}$ and Pt-MO_x types of systems. Most likely, the advanced properties of bimetallic systems are associated with bifunctional nature of $Pt_{0.5}M_{0.5}$ and Pt-MO_x catalysts. Probably, Pt is responsible for CO activation, the second metal is responsible for O_2 activation and the reaction takes place at the Pt-M or Pt-MO_x interface. This hypothesis explains the high selectivity of Pt-Ni and Pt-Co systems at low temperatures and exhibits the important role of “ensemble effect” in the synergism not denying the influence of “ligand effect”.

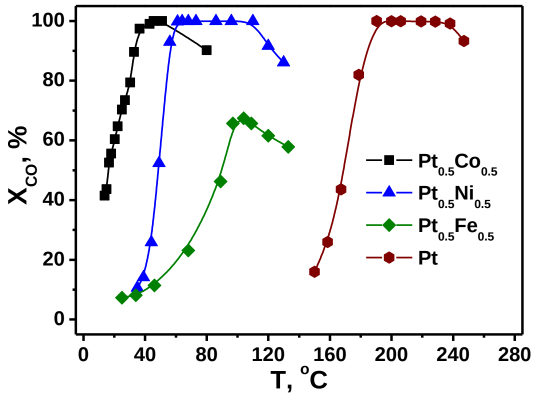

Fig. 1. CO PROX on Pt, $Pt_{0.5}Co_{0.5}$, $Pt_{0.5}Ni_{0.5}$ and $Pt_{0.5}Fe_{0.5}$ nanopowders. Feed gas (vol. %): 1 CO, 1 O_2 and H_2-balance. WHSV: 80000 $cm^3g^{-1}h^{-1}$

The $Pt_{0.5}Co_{0.5}$ and Pt-Co_3O_4 catalysts were studied in more details as the most active ones. Kinetic study was performed and generally approved the made assumptions. Additionally, the structure evolution of $Pt_{0.5}Co_{0.5}$ and Pt-Co_3O_4 nanopowders under CO TOX and PROX conditions was studied by XRD *in situ*.

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Resonant Active Sites in the Catalytic Ammonia Synthesis

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The most of catalytic surfaces exhibit activity only at specific ensembles of near-surface atoms according to the concept of active sites [1]. Surface defects of different origin, chemical nature and morphology play a crucial role in heterogeneous catalysis being the active sites for target reactions, impurities accumulation, etc. The importance of a topic and the lack of quantitative considerations have encouraged this report highlighting a realistic model for examination of surface defects as specific centres for the catalytic ammonia synthesis [2].

Sum of bonds Σ lost by n adjacent surface atoms M forming the M_n site, as compared to the bulk atoms, and enthalpy of local adsorption or reaction is taken as a descriptor for structure and activity of M_n site, respectively. Comparative study have been performed by the Method of Interacting Bonds [3] for M_n sites (n = 1-5) and revealed opposite dependences for the enthalpy of the adsorbed N atoms and NH species formation as a function of Σ on basal planes of Pt, Rh, Ir, Fe, Ru and Re; such behaviour has resulted in volcano curves for the catalytic activity vs. Σ since the product yield under ammonia synthesis is determined by the combination of these reactions. Each maximum in a volcano curve determines the optimal Σ value, and then the resonant catalytic centre on a given metal in close agreement with relevant experimental data. Indeed, the highest activity of particular Fe and Ru single crystals among others is attributed to the specific C_7 and B_5 site; according to calculations, C_7 and B_5 centre is 100 and 50 times more active than site at the fcc (111) and hcp (0001) plane, respectively. The relative activity of most active sites is in proportion $5.0\times10^{-5} : 4.5\times10^{-3} : 1 : 2.5 : 3.0 : 1080 : 2270$ for a sequence of Pt_4, Rh_4, Fe_4(fcc), Ir_4, Fe_{2-5}(bcc), Ru_2 and Re_2, respectively. Noble metals are much less active than Fe- and Ru-based catalysts, because too high Σ values disable resonant sites on basal planes of noble metals due to geometric reasons. Meanwhile, M_3 centres provided by small Pt, Ir and Rh clusters have large enough Σ and exhibit 10^3-10^5 times higher activity compared to (111) plane. In turn, too low Σ values prohibit resonant M_{3-4} sites on Ru and Re, whereas the steric ban becomes overcame in their alloys with noble metals, which theoretical activity up to 10^7 times exceeds that of the pure Pt, Rh or Ir. Similar approach can be useful for other catalytic systems.

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OP-27

RUSNANOtechnological perspectives

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RUSNANO Corporation includes RUSNANO Open Joint Stock Company investing in innovative nanoindustry projects, RUSNANO Management Company LLC responsible for management of the assets, and Fund for Infrastructure and Educational Programs focusing on nanotechnology infrastructure formation and human resources development.

As part of the investment activity, RUSNANO is investing its financial resources, attracting the resources of private investors, taking part in management of its projects and thereby contributing to the development of the domestic nanoindustry. The company invests in wide array of projects, as nanomaterials and surface modification, optics and electronics, medicine and pharmaceutics, energy effectiveness and alternative energy, biotechnology, construction materials and others. During the period 2010-2016, project companies launched 77 new manufacturing facilities with financial support from RUSNANO. Total amount of projects supported by RUSNANO is 107. The company has several joint projects based on nanostructured catalyst technology. RUSNANO partners are the biggest caprolactam producer JSC KuibyshevAzot, largest oil refiner Gazprom Neft P JSC, manufacturer of air purification systems AirLife.

To be financially supported, the project should meet a set of requirements such as nanotechnology attitude and maturity stage of project development (completed R&D stage). The applicant may submit a request for project co-financing by filling in the standard forms on the official site www.rusnano.com. An application for co-financing will pass through several steps including entry review, science and technology expert evaluation and investment evaluation. After a project has been approved, the parties proceed to legally binding documents signing and project financing. Then, as soon as a project is able to function independently, RUSNANO sells its shares to invest the proceeds in other projects.

Another area of RUSNANO activity is connected with stimulating of nanotechnology infrastructure building, popularization of nanotechnology and development of professional education. The Fund for Infrastructure and Education programs is organizing tenders to create Nanotechnology centres and Engineering companies, forming programs for engineers and senior executives of nanotechnology companies, developing the professional standards for advanced engineering professions and arranging special events.

KEYNOTE LECTURES

School-Symposium of young scientists
“*In situ* and *operando* studies of the catalytic reactions”

KLs-1

Active centers in heterogeneous catalysts: formation and study with *in situ* methods

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In the recent years a widespread currency in heterogeneous catalysis has been gained by the fundamental approach to the development of the new catalytic systems, which differs from the traditional empirical strategy in that the molecular design (controlled synthesis) of the active component is preceded by an in-depth study of the mechanisms of the catalytic reactions and structure of the active centers. Evidently the efficiency of this approach depends essentially on the level of development of the physical methods for studying the solid, including, first of all, the surface sensitive methods underlying such field of research as Surface Science.

More than thirty years of use of the physical methods of the surface study significantly advanced the understanding of such phenomena as chemisorption, interaction in the adsorption layers, the chemical reactions on the surface of the solid. However, information registered in the conditions of Surface Science experiments ($P < 10-4$ Pa) may have little in common with the real surface of a working catalyst ($P > 102$ Pa). To solve this problem the researchers lately undertake the numerous attempts to develop some new or modernize the existing methods to study of the catalyst surface in order to conduct the experiments at a pressure of real catalysis. The methods able to work at high pressures list polarization-modulation infrared reflection absorption spectroscopy (PM IRAS) and sum frequency generation spectroscopy (SFG), scanning tunnelling microscopy (CTM) and atomic force microscopy (AFM), and some others. A special place in this list belongs to the methods of absorption of the X-rays (XANES and EXAFS) as well as X-ray photoelectronic spectroscopy (XPS), which attracts a special attention of the researchers due to its universality.

The given lecture presents a review of the studies of the structure of active centers of the supported metal catalysts immediately in the course of the catalytic reaction, i.e. in situ. The reaction of epoxidation of ethylene and oxidation of hydrocarbons are used to demonstrate how the reaction medium changes the chemical and phase state of the active component, and finally forms new adsorption species. The results in this work show that the nature of the active centers performing the catalytic reaction can be determined only when the characterization of the catalyst surface is accompanied with the testing of the catalytic properties (activity and selectivity) by the methods of mass-spectrometry or gas chromatography.

KLs-2

Raman spectroscopy, a convenient tool for operando study of catalysts and for real-time monitoring of catalysts

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The relationship between catalyst structure and reactivity/selectivity remains the most important question in heterogeneous catalysis because such fundamental information would allow for rational design of advanced catalysts. Catalyst surfaces are dynamic and the environmental conditions (T, P, and gas or liquid composition) shape their structure. Consequently, it is critical to establish structure-performance relationships for catalysts operating under relevant reaction conditions given their dynamics.

In situ spectroscopy of heterogeneous catalysts has been practiced for over 60 years and is an invaluable approach for characterizing catalytic materials over a wide range of environmental conditions. In situ characterization studies have allowed scientists to observe catalysts under controlled conditions; however they fall short of providing a direct relationship between catalyst structure and performance because of the absence of corresponding reaction product analysis. The term operando is Latin for "working" and first appeared in the catalysis literature in 2002. Simultaneous time-resolved spectroscopy and online product analysis make it possible to directly relate the catalyst s structure with catalyst performance. In a longer-term perspective, the operando concept was around long before its name. Boreskov and coworkers reported the first operando EPR study in 1966 of vanadium oxide-based catalysts for the oxidation step of SO_2 to SO_3 in the manufacture of sulfuric acid.

The lecture will focus on the potential of Raman and infrared spectroscopy for real-time operando study of supported oxides and support-stabilized nanoscaled oxides during oxidation reactions (parafins to olefins and nitriles) and environmental catalysis (NOx remediation), ranging from fundamental approaches on powder catalysts to honeycomb shaped catalysts. The use of Raman spectroscopy for real time reaction monitoring is also presented.

Acknowledgment. This work is supported by the Spanish Ministry Grant CTQ2014-57578-R.

SHORT ORAL PRESENTATIONS

School-Symposium of young scientists
"*In situ* and *operando* studies of the catalytic reactions"

OPs-1

Pathways of methane conversion on Zn-modified ZSM-5 zeolite revealed with in situ solid-state NMR spectroscopy

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Direct catalytic conversion of methane to more valuable chemicals is one of the important challenges nowadays [1, 2]. Zn-modified zeolites attract much attention from scientific and industrial points of view due to approved evidences for their activity in methane conversion to higher hydrocarbons [3, 4]. The key point in the understanding of such activity is the initial stage of methane transformation, i.e. the activation of methane via an interaction with the surface zinc sites. However, there is an apparent controversy in literature about possible mechanism of methane activation. It is stated that methane dissociation on Zn^{2+} sites is realized via “alkyl” pathway [5] or leads to the surface methoxy species formation (“carbenium” pathway) [6]. Therefore, this work aims to address the issue of methane activation on Zn^{2+}-modified zeolite H-ZSM-5. Particularly, a careful comparison of methane transformation in nonoxidative conditions and in the presence of molecular oxygen has been performed that gives an opportunity to understand whether the activation of methane in nonoxidative conditions on Zn^{2+} sites leads to surface methoxy species or the formation of zinc-methyl species is only possible. Following this methodology, methane transformation on Zn^{2+}-exchanged H-ZSM-5 zeolite has been carefully investigated. To monitor surface intermediates formed from methane as the result of its activation by Zn^{2+}-sites, advanced methods of *in situ* solid-state NMR spectroscopy have been applied. ^{13}C CP/MAS NMR spectroscopic data clearly and evidently demonstrate that the methane activation on Zn^{2+}-modified ZSM-5 zeolites affords exclusively zinc-methyl species, while the presence of admixed molecular oxygen in methane can provide the formation of Zn-methoxy species. Hence, the obtained results give the opportunity to answer the question about the possible ways of methane activation and conversion to more valuable chemicals.

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The nature of heterogeneous catalyst active sites responsible for the pairwise H_2 addition: *in situ* study by PHIP technique

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Parahydrogen induced nuclear polarization (PHIP) is a powerful technique for the mechanistic study of hydrogenation reactions [1]. This approach exploits the high nuclear spin order of parahydrogen, the spin isomer of H_2. PHIP technique can enhance the NMR signal significantly (up to 10^5 times) on the condition that the hydrogenation reaction proceeds in a pairwise manner of H_2 addition. Due to the PHIP signal amplification it becomes possible to *in situ* determine the possible reaction intermediates and to obtain the valuable mechanistic and kinetic information of catalytic reactions under investigation.

However, since the discovery of the PHIP effect [2], this method has mainly been used for the mechanistic study of homogeneous hydrogenation reactions catalyzed by various transition metal complexes. Nevertheless, in 2008 [3], a group of researchers from ITC and BIC SB RAS for the first time demonstrated the possibility of PHIP effects observation in the catalytic hydrogenation over supported metal catalysts (heterogeneous catalysts). This observation clearly indicates that in addition to the recognized Horiuti–Polanyi mechanism of hydrogenation, implying dissociative chemisorption of hydrogen, there is another pathway of hydrogenation in which both H atoms of parahydrogen molecule ends up into the same product molecule. Nevertheless, the nature of active sites of supported metal catalysts which can add molecular hydrogen to the unsaturated substrates in a pairwise manner is unclear.

Therefore, we have attempted to get some insight into the heterogeneous pairwise hydrogen addition phenomenon over heterogeneous catalysts in this work. We studied the structure of active sites responsible for the pairwise hydrogen addition. PHIP was utilized to demonstrate the strong metal-support interaction (SMSI) effect for Pd/TiO_2 catalyst that allowed establishing the effect of catalysts reductive pretreatment on the structure of active sites which are responsible for pairwise hydrogenation [4]. Moreover, we have investigated the influence of oxidative/reductive pretreatments for TiO_2 supported catalyst via PHIP effects detection [5]. It was shown that the oxidation or the reduction of the catalysts impact dramatically on the overall catalytic activity and, more importantly, on the selectivity toward pairwise hydrogen addition to a substrate.

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ESR *in-situ* – effective tool to study the active intermediates occurring at the metal-oxide interface of the Au/Al_2O_3 catalyst

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$Au/\gamma\text{-}Al_2O_3$ catalysts are known to provide high chemoselective hydrogenation of nitroarenes to aniline. One of the suppositions implies the active sites for catalytical hydrogenation on the surface of Au/Al_2O_3 are located at the $Au\text{-}Al_2O_3$ interface [1-3]. Unfortunately, there is still no any direct experimental evidence for the active sites localization due to the absence of the adequate experimental tools that could provide the appropriate data *in situ*. It makes the exact mechanism of chemoselective hydrogenation of nitroarenes to anilines over Au/Al_2O_3 catalyst is still unclear.

Some authors applied ESR technique to study the interaction of Al_2O_3 surface with nitroaromatic compounds. For example the behavior of $\gamma\text{-}Al_2O_3$ based systems in the liquid solution of TNB in toluene was investigated few years ago [4]. It was shown, that electron transfer takes place between TNB and –OH group of the $\gamma\text{-}Al_2O_3$ surface.

Here we demonstrate the ESR method *in situ* allows us to study the active intermediates occurring at the metal-oxide interface of the catalyst. We report the data on the mechanism of hydrogenation of nitrobenzene over Au/Al_2O_3 catalyst via ESR *in situ*.

The ESR technique was applied to reveal the radicals formed at the Au-alumina interface as the result of the interaction of nitrobenzene with active sites on the catalyst surface. The spectra registered are attributed to the immobilized radicals while there is no detectable ESR signal is observed for the solution over the samples. It was proved the radicals adsorption occurs only at the $Au\text{-}Al_2O_3$ interface, while nor “pure” alumina neither the surface of gold nanoparticles is capable to form a radical species in the reaction conditions in contact with nitrobenzene. The nitro-radicals detected should be considered as the intermediate species for the catalytic hydrogenation of nitrobenzene to aniline. It was confirmed providing simultaneous GC-MS analysis of reaction mixture with the registration of ESR spectra *in situ* which displayed the severe drop of the resonance absorption intensity during the reaction.

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OPs-4

Mechanisms of Biomimetic Iron-Catalyzed Enantioselective Epoxidations

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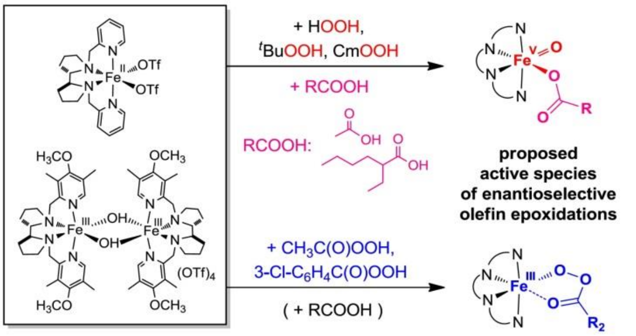
The search for robust and selective biomimetic catalysts that are capable of oxidizing organic substrates in the same fashion as metalloenzymes has been a challenging task for years. The detection and characterization of the active species of biomimetic catalyst systems, which can also provide important insights into biological pathways, is a hot topic of oxidation chemistry. Chiral bipyrrolidine-derived aminopyridine (PDP) structure appeared as simple and versatile ligand framework, the resulting complexes, studied herein (Scheme 1), being among the most efficient and selective iron-based bioinspired catalysts. The presented study was mostly aimed at the nature and reactivity of active species conducting enantioselective olefin epoxidations, since these data is a key to understanding the mechanism of catalytic performance.

In this work, we have examined the mechanistic landscape of the Fe(PDP) catalyst family with various oxidants: H_2O_2, organic hydroperoxides and peracids. The combined EPR spectroscopic, enantioselectivity, Hammett, *Z*-stilbene epoxidation stereoselectivity, and ^{18}O labeling data witness that the same oxoiron complexes $[(L)Fe^{V}{=}O(OC(O)R)]^{2+}$ are the actual epoxidizing species in both the catalyst systems $(L)Fe/H_2O_2$/carboxylic acid and (L)Fe/AlkylOOH/carboxylic acid. On the contrary, in the systems $(L)Fe/R^2C(O)OOH$ (R^2 = CH_3 or 3-Cl-C_6H_4), the epoxidation is predominantly conducted by the acylperoxo-iron(III) intermediates $[(L)Fe^{III}(OOC(O)R^2)]^{2+}$, in a concerted fashion (Scheme 1).

The electronic structure of the iron-oxygen intermediates responsible for catalytic transformations has been found to strongly depend on the structure of the added carboxylic acid RCOOH. For RCOOH with primary and secondary α-carbon atom, the active species exhibit EPR spectra with large *g*-factor anisotropy ($g_1 = 2.7$, $g_2 = 2.4$, $g_3 = 1.7$), whereas for those with tertiary α-carbon atom, the active species display EPR spectra with small *g*-factor anisotropy ($g_1 = 2.07$, $g_2 = 2.01$, $g_3 = 1.96$). The EPR spectra of the latter intermediates are very similar to those of the intermediates previously assigned to oxoiron(V) species. The systems featuring intermediates of the 2nd type ensure higher enantioselection in the epoxidation of electron-deficient olefins.



Scheme 1. Active epoxidation species proposed to operate in the catalyst systems with different oxidants

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Operando approach to investigations of oscillatory behaviour in catalytic oxidation of light alkanes over nickel

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One of the most interesting and unusual phenomena of catalysis is the self-sustained reaction-rate oscillations [1]. To date approximately 70 oscillating heterogeneous catalytic systems are known. Among them are oscillations in the oxidation of light alkanes over transition metals which attract special attention in the last years due to practical importance [2]. *Operando* investigation of such kinetic instabilities is a challenge for researchers because it demands using special approach and special setups. Nevertheless, the obtained information about the origin and the mechanism of these oscillations can open the possibility to perform the catalytic processes more effectively using the unsteady-state operation.

As illustration of using *operando* approach we present the investigation of self-sustained reaction-rate oscillations in the oxidation of methane and propane over nickel. To study the oxidation of methane over nickel at atmospheric pressure X-ray diffraction and mass spectrometry were chosen. Near ambient pressure X-ray photoelectron spectroscopy and mass spectrometry were used to study the oxidation of propane over nickel.

Operando XRD/MS experiments were carried out at the “High Precision Diffractometry II” station at Siberian Synchrotron and Terahertz Radiation Center (Novosibirsk, Russia). The diffractometer is equipped with high temperature reaction chamber that allows observing the diffraction patterns within temperature range from RT to 900 °C in the reactant mixture at atmospheric pressure. *Operando* XPS/MS experiments were carried out at the ISISS station at BESSY-II (Berlin, Germany). The setup is equipped with a special heating system that allows simultaneously heating the sample within temperature range from RT to 900 °C in the reactant mixture at pressure up to 20 mbar and obtaining the XPS spectra of the catalyst surface.

It was shown that in temperature range of 650-900 °C in the oxygen-deficient conditions in these systems the self-sustained oscillation of relaxation type was observed. The oscillations of the reaction rate accompanied with catalyst temperature oscillations. It was found that in the high active state the nickel is in the metallic state as clearly evidenced by both XRD and XPS. Transition to low active state accompanied the formation of NiO layer on the catalyst surface. Thus, *operando* approach enables us to establish that the origin of oscillations in the systems is determined by periodic oxidation/reduction of nickel.

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0001 for Boreskov Institute of Catalysis.

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In situ XRD study of self-sustained reaction-rate oscillations in the oxidation of methane over palladium

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Many heterogeneous catalytic reactions show an unusual behaviour including rate oscillations, spatiotemporal patterns and deterministic chaos [1]. Among the various phenomena the self-sustained rate oscillations in the oxidation of light alkanes over transition metals (Ni[2], Pd[3], Co[4]) have become a focus of research over the last two decades. In situ investigations of such kinetic instabilities open new opportunities to study the mechanisms for these catalytic reactions. In this work we studied the self-sustained rate oscillations in the oxidation of methane over polycrystalline supported and single crystal Pd catalysts at atmospheric pressure using an X-ray diffraction technique and mass spectrometry.

In situ XRD/MS experiments were carried out at the “High Precision Diffractometry II” station at Siberian Synchrotron and Terahertz Radiation Center (Novosibirsk, Russia). The diffractometer was equipped with high temperature reaction chamber XRK-900 (Anton Paar GmbH), that allows measuring the diffraction patterns within temperature range from RT to 900 °C in different environments, and quadruple-type gas analyser UGA-100 (Stanford Research Systems Inc.) to analyse the products and reactants. The time-resolved XRD experiments were performed using position sensitive parallax-free linear OD-3M detector (BINP SB RAS) [5]. X-ray wavelength of 1.642 Å was set by a single reflection from flat perfect crystal monochromator Si(111). Mass flow controllers SEC-Z500 (Horiba Ltd.) were used to supply the feed gas composition at selected proportions.

According to the results the periodic changes of XRD reflexes intensities corresponding to Pd, PdO, and PdC_x phases were accompanied by synchronous variations of the catalyst temperature. In the low active state the catalyst surface was oxidized, and transition to the high active state occurred simultaneously with the formation of metallic phase. In addition to the latter we also observed formation of PdC_x phase with larger lattice parameter on the catalyst surface.

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OPs-7

In Situ and Ex Situ Studies of Bimetallic Catalysts Activation for Multi-walled Carbon Nanotubes Growth

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Multi-walled carbon nanotubes (MWCNTs) are considered to be promising material for a number of applications due to their unique mechanical, structural properties, and high electrical conductivity. These properties mainly depend on the diameter distribution and defect concentration, which, in turn, defined by on the catalyst nature and growth conditions. The formation of the catalytic species and nucleation of the carbon deposits determine the selectivity and activity of nanotube growth process. Thus, the investigation of the catalyst active component formation and carbon nucleation is extremely important for the design of selective processes of MWCNT production.

In the present work the formation of the active component of the bimetallic catalysts during MWCNT growth was studied using *in situ* and *ex situ* synchrotron radiation XRD. According to in situ SRXRD data, at least four processes can be distinguished during the induction period, such as active metal reduction, metal particles growth and/or agglomeration, their saturation with carbon and MWCNT nucleation. These processes follow each other, except the second and the third one which occur simultaneously. For the first time we have obtained data confirming the stepwise formation of Fe-Co bimetallic alloy. It was found that the cobalt particles are formed at the first stage of catalyst reduction. These primary particles promote the reduction of Fe species with the subsequent formation of the alloy. Mono-component Fe catalyst demonstrates the simultaneous formation of Fe–C alloys with subsequent transformation into stable iron carbide. The *in situ* activation of the bimetal Fe–Co catalysts supported on Al-based oxides and CaO leads to the formation of highly dispersed alloyed particles. Meanwhile, the stable carbide formation for such systems is not observed. The absence of stable carbides promotes effective carbon diffusion through metal particle providing much higher activity of multicomponent Fe–Co catalysts compared to that of Fe catalysts. According to the XRD data, catalyst active component (alloy particles) is solid or at least contains crystalline core during CNT growth. We have observed carbon species tend to concentrate at the surface of active particle leading to negligible concentration in the bulk. The results obtained by XRD in combination with other physical methods (*ex situ* HRTEM, internal field ^{59}Co NMR, *in situ* XPS, gas chromatography etc.) have been used for the development of kinetic model and the optimization of the synthesis conditions to produce MWCNT with controlled properties in a fluidized bed reactor.

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OPs-8

In situ XRD and XPS study of the reduction process of mixed Mn-Zr oxide catalysts of CO oxidation

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Mn-Zn mixed oxides can effectively catalyze the gas-phase oxidation of hydrocarbons or chlorcarbons. Although there is agreement that the catalytic activity of these catalysts is determined by their redox properties, the exact mechanism of these oxidation reactions is not clear yet. Mn cations can enter the lattice of ZrO_2 with the formation of solid solutions $Zr_{1-x}Mn_xO_2$, in which lattice oxygen possesses sufficiently high mobility and hence high reactivity. On the other hand, some authors suppose that the active species in oxidation reactions is mobile oxygen that is incorporated in disperse MnO_x rather than lattice oxygen of the solid solution. Moreover, in a reducing atmosphere, a segregation of manganese with the formation of dispersed MnO_x is possible on the surface of the solid solution $Zr_{1-x}Mn_xO_2$.

A series of catalysts based on mixed Mn-Zr oxides with different molar ratios Mn/Zr (Mn/Zr = 0.12, 0.3, 0.4, 0.6, 0.7, 0.90) have been prepared by coprecipitation of manganese and zirconium nitrates and characterized by X-ray diffraction and N_2 adsorption techniques. It has been found that at low Mn/Zr ratios ($Mn/Zr < 0.3$), the catalysts are single-phase solid solutions ($Mn_xZr_{1-x}O_{2-\delta}$) based on a ZrO_2 structure. According to XPS data, manganese in these solutions exists mainly in the Mn^{4+} state. An increase in the Mn content mostly leads to an increase in the number of Mn cations in the structure of the solid solutions, but a part of manganese form Mn_2O_3 and Mn_3O_4 in crystalline and amorphous states. Reduction of these catalysts with hydrogen was studied by a temperature-programmed reduction technique, in situ XRD, and near ambient pressure XPS in a temperature range from 100 to 650 °C. It was shown that the reduction of the solid solutions $Mn_xZr_{1-x}O_{2-\delta}$ proceeds via two stages. During the first stage, between 100 and 500 °C, Mn cations incorporated into the solid solutions $Mn_xZr_{1-x}O_{2-\delta}$ undergo partial reduction. During the second stage, at temperatures between 500 and 650 °C, Mn cations segregate on the surface of the solid solution. In the catalysts with high Mn/Zr ratios ($Mn/Zr > 0.3$), the reduction of manganese oxide was observed: $Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$.

Catalytic synthesis and properties of nitrogen doped carbon nanotubes and nanofibers

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Nitrogen-doped carbons are of great interest for application in catalysis. The use of these materials as supports can increase the activity, change the selectivity and improve catalysts stability in the course of the reactions due to their exceptional properties [1]. In the present work we describe the method of the synthesis of nitrogen-doped carbon nanotubes (N-CNTs) and nanofibers (N-CNFs) by the use of simple standard ethylene-ammonia mixtures and different metal catalysts. We have found that ammonia concentration in reaction mixture is the main factor influencing the content of nitrogen both in N-CNTs and N-CNFs. The nitrogen is incorporated into the main pyridine-like, pyrrolic and quaternary positions in the graphite-like structure. According to TEM N-CNTs have bamboo-like structure while N-CNFs have the preferential herring-bone packing of graphite layers.

EELS spectroscopy combined with HAADF-STEM showed the uniform distribution of nitrogen in N-CNTs and not uniform in the case of N-CNFs. These data were explained by different mechanisms growth of N-CNTs and N-CNFs revealed by the use of in situ XRD study of the metal catalysts during carbons growth. It was demonstrated that nitrogen doping leads to the structure disordering of the synthesized carbons: the increase of nitrogen content is accompanied by the increase of the I_D/I_G ratio in Raman spectra and decrease of the electrical conductivity of the materials. The XRD study showed the formation of ordered defects in N-CNTs while no ordering of defects in N-CNFs was found. The original simulation of the N-CNT structure using the graphitic g-C_3N_4 phase and turbostratic ordering made it possible to propose a new model of the spatially ordered defects in the N-CNT layer, which consist of clusters of carbon vacancies and pyridine-like nitrogen [2].

For the first time N-CNTs and N-CNFs were used for immobilization of catalytically active polyoxometalates (POMs) for selective oxidation of alkylarenes for the synthesis of alkyl-*p*-benzoquinones. It was demonstrated that nitrogen doped carbons are promising solid supports that ensures strong adsorption and molecular dispersion of POMs leading to highly active, selective (up to 99 %) and stable in the course of the reaction heterogeneous catalysts.

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OPs-10

In-situ study of the titanium dioxide aggregation processes in the organic media

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Titanium dioxide has a lot of application in the paint production, photocatalysis, catalysis and others areas of industry [1]. The advanced materials from titanium dioxide with required properties are often size dependent and it is essential to be able to control the particle size, shape, and size distribution. Respectively this needs a detailed understanding and managing of the mechanisms of growth of titanium nanoparticles at their production. Most popular way of nano-sized TiO_2 preparation it is sol-gel synthesis from titanium alkoxides [1]. There is a lot information about mechanism of TiO_2 aggregation in the water media or media enriched by water [1, 2]. In these cases primary mechanism of nanoparticles aggregation is the Ostwald ripening. Nevertheless the question about possible changing of this mechanism at another reaction condition has not studied yet. Changing of water phase on the organic phase can give new possibilities in managing reaction of titanium alkoxides hydrolysis. In our work we studied hydrolysis reaction of titanium butoxide in the butanol-1 media with small quantity of water and HCl as acid catalyst. The atomic ratio titanium butoxide/water is equal 1:8. At current synthesis parameters the water does not form separately phase and present as solution in alcohol. For determination TiO_2 nanoparticles sizes in sols it have been used SAXS and TEM. Comparing to the TEM technique the SAXS method allows to observe nanoparticles in colloidal solutions directly. According SAXS data the TiO_2 nanoparticles have no definite shape and have radii gyration (R_G) values in the range from 1.5 to 6.0 nm. The best fit of the experimental SAXS data has been observed when such particles are described as Gaussian chains. At this time TEM data shown that the TiO_2 particles has a compact shape and sizes from one to dozens nm. We assume that during TEM analysis are changed the particles shape and also some particles agglutinate to each other. The dependence of the R_G values from the time show that in this case particles aggregation are observed noticeably slower than would be expected according to the Ostwald ripening mechanism. We can conclude that in our conditions is observed the coalescence mechanism of particles aggregation. In report will be discussed reasons and features of the mechanism aggregation changing. This effect of aggregation mechanisms switch could be useful for design of new materials based on the titanium dioxide.

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POSTER PRESENTATIONS

PP-1

New direction of refining of gaseous alkanes

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The need for high-octane gasoline with a low content of aromatic hydrocarbons involves the replacement of the high-temperature dehydrocyclisation processing of straight-run gasoline (SRG) on the low-temperature isomerization.

In this work presents the results of research of catalytic transformations of SRG at low temperatures 180-220° on the composite catalysts of the Me/H-zeolite-SO_4^{2-}/ZrO_2, shows the possibility of replacing of high-dehydrocyclization processing (reforming) to isomerisation (izoriforming). We synthesized Me/H-zeolite/SZ composite catalyst systems (Me = Co) and conducted the SRG contacting with these catalysts at 140-220 °C, GHSV = 2.5 h^{-1} at atmospheric pressure in a hydrogen flow (20-40 ml/min). In the temperature range of 180-220° by contact the straight-run gasoline with Me/HZSM-5-SO_4^{2-}/ZrO_2 (M/Z-SZ) catalysts the C_{7+} components are converted (20.8-58.8 %) in hydrocarbons of C_5-C_6 (18.2-48.2 %) containing up to 46-78 % high octane isomers. It was found that the composite catalyst prepared based on HZSM-5 zeolite and containing 2 % SO_4^{2-} in contact with the SRG at 180° allows to reduce the content of high molecular weight hydrocarbons in product to 35 % and to increase the amount of C_5-C_6 hydrocarbons, comprising 56.9 % of the high octane isomers, from 11.0 % to 48.2 %.

Dilution of SRG by gaseous alkanes (GA) leads to the inclusion in the process up to 70 % of gaseous alkanes at conversion of C_{7+} to 63 %.

For clarifying the mechanism of the SRG conversion the model transformation of n-butane, n-heptan and mixtures there of (1:0.3 mol) over M/Z-SZ was studied. The conversion of n-C_7H_{16}, n-C_4H_{10} and their mixture C_7H_{16}:n-C_4H_{10}=1:0,3 have been studied on the composite catalysts $Al_2O_3/SO_4^{2-}\cdot ZrO_2$ (A-SZ) and M/Z-SZ at atmosphere pressure and H_2/hydrocarbon = 3 and 140-200° temperatures. It was found that A and Z do not affect to the isomerization and hydrocracking reactions of n-C_7H_{16} on the A-SZ and Z-SZ. The mixture of C_7H_{16}:n-C_4H_{10} is converted with high selectivity to the isomers of C_5-C_6. It was assumed about the activation mechanism of bimolecular C_{11} intermediate which precede to the formation of the products of this react.

The obtained results show the possibility of co-processing of SRG and gaseous alkanes in the qualitative gasoline, containing no aromatic hydrocarbons.

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PP-2

Effect of A-site cations ordering on catalytic performance of Sr-Gd-Co mixed oxides with perovskite structure

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Substituted rare-earth perovskites display a wide variety of fascinating electric, magnetic, optical and catalytic properties. The perovskite structure allows a large number of ionic substitutions to form A/B-site ordered or completely/partially disordered states giving rise to specific properties not inherent to ABO_3 perovskites. There are numerous studies considering the correlation between nature of B-site cation, physico-chemical properties (including order–disorder phenomena on B-site) and catalytic performance of perovskite catalysts but to the best of our knowledge, there is only limited information on influence of nature of A-site ions and peculiarities of A-site ions distribution on catalytic performance of $A_xA'_{1-x}BO_{3-\delta}$ mixed perovskites.

The aim of the presentation is to summarize our experimental results on oxidative catalytic conversion of methane over Sr-Gd-Co perovskites to reveal the reason of the influence of structural A-site disordering on catalytic properties. Two sets of monophase perovskite samples $Sr_xGd_{1-x}CoO_{3-\delta}$ (x = 0.5, 0.8 and 0.9) with different arrangement of Sr/Gd over A-site will be presented: metastable cubic and stable tetragonal perovskite phases, with disordered and ordered Sr/Gd distribution, accordingly. Activity and selectivity of the samples in the reaction of CH_4 oxidative conversion at 400-800 °C will be given, as well as the results of kinetic studies of methane oxidation, O_2 TPD and TPR in hydrogen, non-stationary DSC-TG measurements of mobile oxygen amount and enthalpy of its removal.

It will be shown that cubic perovskite phases with disordered Gd/Sr cations are up to five times more active in the reaction of CH_4 deep oxidation and less selective in reaction of oxidative conversion to ethylene+ethane than tetragonal perovskite phases with ordered distribution of Gd/Sr over the A-sites of the crystal lattice [1]. The difference in catalytic performance is attributed to weakly bound mobile oxygen, presented on A-site of disordered perovskites, as a result of the structure-directed changes of the amount of mobile oxygen in the crystal lattice and its thermochemical properties.

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PP-3

Formation of branched polyethylene over 2-iminopyridine nickel(II) complexes under homogeneous and heterogeneous conditions

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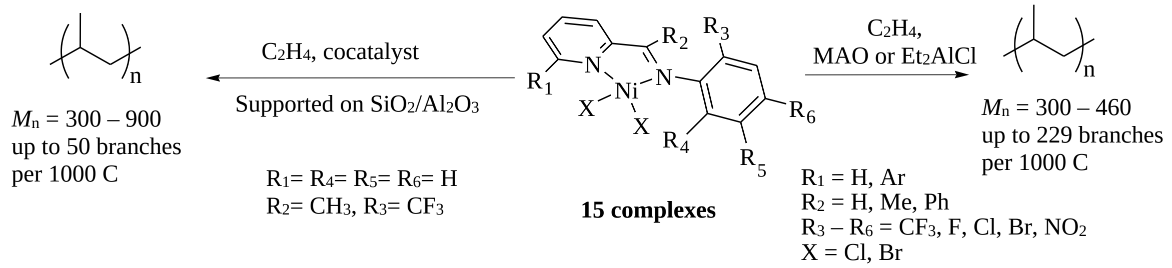
Polyolefin production is one of the major large-scale industrial processes. Most part of commercial polyethylene (PE) and polypropylene (PP) is obtained by traditional heterogeneous Ziegler-Natta catalysts. However, the share of special varieties of polyolefins produced using single-site catalysts (metallocene and non-metallocene) has increased remarkably in the last few years [1]. Such polymers exhibit more defined microstructures, controlled molecular weight distributions, improved mechanical, optical, and other properties.

Among nickel(II) based post–metallocene polymerization catalysts [2], nickel(II) complexes with 2–iminopyridine ligands are of great importance because these complexes are able to produce highly branched polyethylenes, having low molecular weight and narrow molecular weight distribution. Significantly, such PE waxes exhibit interesting performance features in specialty applications and could be used as lubricant additives [3].



In this work, 15 nickel(II) complexes with 2-iminopyridine ligands, bearing electron-withdrawing substituents, have been synthesized, and displayed the highest reported activity for ethylene polymerizations over iminopyridine nickel catalysts. Complexes with unsubstituted or aryl-substituted 6th position of pyridine ring (R_1 = H, Ar) and *o*–trifluoromethyl group at phenyl ring appeared highly active (up to $6.6 \cdot 10^6$ g PE $(\mathrm{mol \cdot Ni})^{-1}$ $\mathrm{h}^{-1} \cdot \mathrm{bar}^{-1}$), affording branched low-molecular-weight PEs (86-229 branches per 1000 C), with narrow molecular weight distribution (M_w/M_n = 1.7-2.6). Supported catalysts demonstrated higher temperature stability (up to 80 °C), affording PE with broader molecular weight distribution (M_w/M_n = 6.2-45) and lower level of branching than the homogeneous catalyst.

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PP-4

New method of utilization of sulfur-containing exhaust gases of factories

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Now for the purification of hydrocarbon gases from H_2S and CO_2, and also utilization of exhaust gas emissions of sulphides is applied the numerous processes based on chemical, physical, or physical and chemical interacting of components. On the basis of the above-stated purpose of the given work is rather analytical studying literary information on the purification of sulfur-containing gases from H_2S, CO_2, development of process flowsheet on the aftertreatment of exhaust gas, emissions of obtaining system of sulphur. The process for the purification of gas harmful sulfur-containing emissions of a chemical complex was carried out with the application of new reagents, i.e. sulfur oxide absorbers, as Ca $(OH)_2$.

Table 1. The influence of content of sulfur dioxide on the purification depth

№	Content of sulfur dioxide, %		Chemisorption	Purification depth, % vol.
	Before purification	At the beginning of purification (in 5 minutes)		
1	0,65	0,26	0,39	60,0
2	0,44	0,12	0,32	73,0
3	0,33	0,009	0,32	97,3
4	0,26	0,005	0,25	98,1

Interacting velocity of SO_3 with aqueous solutions $Ca(OH)_2$ (W) is defined on the equation: $W = V/C \cdot \tau$, sm^3 ($\% \cdot$ sec.) where V-volume absorbed SO_3, sm^3, N-concentration of solution of Ca $(OH)_2$, τ - duration of experience, sec. In table 2. Results of measurement of interacting velocity of SO_3 with various concentration water to solutions of $Ca(OH)_2$ are resulted.

Table 2.

№	Concentration $Ca(OH)_2$, %	W ($sm^3/\% \cdot$ sec.)	№	Concentration $Ca(OH)_2$, %	W ($sm^3/\% \cdot$ sec.)
1	0,5	0,85	5	4,0	0,92
2	1,0	0,94	6	5,0	0,90
3	1,5	1,00	7	8,0	0,89
4	2,0	0,98	8	10,0	0,80

On the basis of the resulted data in tab. 2 it is possible to assert that separation efficiency of exhaust gas emissions from SO_2 and SO_3 is influenced by concentration of an applied aqueous solution of $Ca(OH)_2$. At raise of a solution strength of $Ca(OH)_2$ from 0,5 % to 4,0 % interacting velocity of SO_3 with aqueous solutions of $Ca(OH)_2$ accordingly makes 0,85-1,0 $sm^3/(\%$ сек). Further increase in the concentration of $Ca(OH)_2$ leads to decrease in the velocity of interacting to 0,80 $sm^3/\% \cdot$ sec.

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PP-5

Development of Intermetallic Catalysts for CO_2-CH_4 Reforming

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A study of intermetallide supported Pt [1], Mo catalysts for carbon dioxide reforming of methane was investigated and compared with the industrial catalyst tested under same reaction conditions. In this work we propose a new type of catalytic systems on the base of Ni_3Al intermetallic compound without and with modification by noble and base metals.

The catalysts were prepared by self-propagating high temperature synthesis [1]. Modification was performed by means of ion implantation using Mevva-V.RU (Metal Vapour Vacuum Arc) set-up (originally designed in Lawrence Berkeley National Laboratory (USA)). Catalysts were characterized by XRD (in situ and ex situ), DTA-TG, SEM+EDS, HRTEM+EDS and XPS. Activity testing has been performed with fixed bed reactor equipped with a gas chromatograph at a reaction temperature of 600-900 °C under atmospheric pressure and the reactant molar ratio of CH_4:CO_2 of 1. *In situ* XRD experiments were carried out in the VEPP-3 station of Siberian Synchrotron and Terahertz Radiation Center of Budker Institute of Nuclear Physics of SB RAS.

This work concentrates on a new type of the catalysts for CO_2-CH_4 reforming, or dry reforming of methane (DRM). Instead of traditional supports on the base of metal oxides, we propose to use material on the base of Ni_3Al superalloy because of its excellent thermal conductivity, high temperature strength, good corrosion/oxidation resistance and mechanical tics. In severe redox DRM atmosphere at high temperature (800-900 °C), Ni_3Al matrix undergoes weak phase transformations, supplying pure Ni nanoparticles, served as the active sites for methane and carbon dioxide activation.

The unmodified Ni_3Al catalyst revealed good activity in DRM at temperatures of 600-900 °C. Nevertheless, this catalyst undergoes partial deactivation because of carbon deposition. Introduction of small amount of Pt and Mo significantly decreases the coking rate and causes an increase in specific activity and a rise in the catalysts resistance to coking. Catalytic activity results have shown that in the case of Ni_3Al intermetallic samples the presence of Pt strongly enhances the catalytic performance, with an effect which increases with the rise of the Pt content.

Pt-implanted catalysts have two main advantages in comparison with unmodified Ni_3Al: (a) they work without the apparent activation stage, (b) they are stable during 120 hours without obvious deactivation.

In general, this work has demonstrated the novel possibilities of catalyst synthesis by means of SHS and modification of the surface with ion implantation.

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PP-6

The formation of nanoscale magnetocontrollable catalysts of coal hydrogenolysis

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We elaborate the methods of deriving of nanoscale carbon-mineral magnetic composites on the basis of the magnetite (Fe_3O_4) and greigite (Fe_3S_4) and their use in the process of coal hydrogenolysis into liquid hydrocarbonic products.

Macromolecules of the explored Kazakhstan coals consist of bunches of the condensed aromatic rings. About three rings on the average included in into each bunch for coal of a medial stage of a metamorphism. These bunches are bounded by hydroaromatic and heteroaromatic structures which one determine the space tridimensional disposing of a macromolecule. The volume of open pores in the explored coals is proportioned as follows: the volume (cm^3/g) at diameter < 1,2 nanometers (micropores) compounds 0,02-0,07; at diameter 1,2-3 nanometers (mesopores) – 0,04-0,1, over 30 nanometers (macropores) – 0,009-0,09. At the tinging of the coal grinded till 5-10 micron by the prepared in advance magnetic fluids on the basis of the magnetite (Fe_3O_4), synthesised by the method of chemical sedimentation or of the greigite (Fe_3S_4), gained by the method of thermal decomposition of the iron (II) acetate of and thiurea, using a hydrocarbon with t_{boil} 350-380 °C in the quality of a disperse medium and a stabiliser, we gained the magnetic composite characterised by the equilibrium distribution of magnetic material on a coal surface with particle size from 20 to 100 nanometer. Adsorption isotherms of the coal permeated with a magnetic fluid allow to ascertain the mechanism of a capillary sorption at filling up with a fluid of mesopores namely.

As distinct from magnetite (Fe_3O_4) greigite (Fe_3S_4) is strong inferior to the magnetite on the magnetic characteristics (a saturation magnetisation, a remanent magnetization, a coercive force). However with the size decrease (from 10 nanometers and less) nanoparticles of the greigite also are inclined to a superparamagnetic state, as well as the magnetite nanoparticles. The linear dependence of magnetisation from concentration of magnetic material is determined.

The obtained magnetic composites are tested in the process of coal hydrogenolysis. The effects demonstrate that at the temperature 410 °C and the pressure 5,0 MPa the liquid yield is enlarged from 54,8 to 62,5 % with the augmentation of the concentration of the Fe_3O_4 at a carrier from 6,0 to 12,0 mass. %. the liquid yield compounds 30,4 % in the experiment without the active phases depositing, and the additive of the active phases leads to augmentation up to 62,5 %. The incorporation of cobalt compounds ($Co(Fe_2O_4)$ in the composition of the catalyst leads to the increase of liquid yield up to 75,0 %. At that the yield of petrol fraction enlarged up to 15,8 %.

Operando studies on powder and shaped supported vanadia catalysts for environmental catalysis

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Catalysis cannot be understood without spectroscopy, which has to be made during catalytic operation so that we may connect both structure and performance; determining the states and interplay of catalyst sites and reacting molecules. An *operando* study on powder and shaped vanadium oxide based catalysts is reported to understand selective catalytic reduction of NOx with ammonia (SCR). The SCR process has been employed industrially for decades; it is generally accepted that the reaction follows and Eley-Rideal type mechanism at 200°C; however, the role of NH_3 interaction with molecularly dispersed vanadia, and the interplay with water and NOx species is not clearly assessed yet. Raman and infrared spectroscopies provide fundamental molecular information on the states of the catalyst and surface species, while EPR provides additional insight on the oxidation states of vanadium species. The combined use of characterization of the catalysts at work provides further insight, but their coupling is complicated by the inherent constraints of each technique, this work will present our progress in understanding powder and honeycomb shaped catalysts, as well as the combination of operando methodologies.

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PP-8

EPR Characterization of Surface Electron-Acceptor Sites in the Course of a Catalytic Reaction

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The existence of electron-acceptor sites with electron affinities ~ 7 eV in large quantities on the surface of Al_2O_3 and many other oxides is quite remarkable. Electron-acceptor sites of different strengths can be characterized using aromatic probes with different ionization potentials [1]. It was shown earlier that the catalytic activity in dehydrochlorination of 1-chlorobutane over nanocrystalline MgO substantially increases with time due to the MgO modification with chlorine [2]. In this study we characterized weak electron-acceptor sites formed during 1-chlorobutane dehydrochlorination over several oxide catalysts using perylene as a spin probe, and found a good correlation between their concentrations and the catalytic activity, which substantially change due to the surface modification with chlorine.

The catalytic reaction of 1-chlorobutane present in the gas flow was performed in an EPR sample tube. Its conversion to a mixture of butenes was monitored by gas chromatography. After the reaction was carried out for the desired time, the sample was quickly cooled to room temperature and filled with a solution of perylene in toluene. Then the concentration of the formed radical cations was measured by EPR.

The catalytic activity of nanocrystalline MgO, Al_2O_3 and ZrO_2 was found to increase significantly during the first ~ 30 minutes of 1-chlorobutane dehydrochlorination reaction, which is accompanied by modification of the oxide surface with chloride ions, before reaching a steady state. The concentration of electron-acceptor sites was also found to grow during this period of time due to the surface chlorination following the increase of the catalytic activity. So, a good correlation was observed between the catalytic activity and the concentration of the studied electron-acceptor sites.

The suggested method can be used for to monitor changes in the concentration and strength of active electron-acceptor sites on the catalyst surface in the course of any catalytic reaction. It is important to study possible correlations between the concentrations of electron-acceptor sites and catalytic activity of various catalytic reactions believed to take place on surface acid sites to elucidate the possible role of electron-acceptor sites in these reactions.

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PP-9

FTIR-spectroscopic studies of H_2O adsorption on the surface of γ-Al_2O_3

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Alumina is a valuable material for chemical and petrochemical indistries, and is widely used as a catalyst and/or catalyst support. γ-Al_2O_3 is a typical Lewis solid acid. It is generally assumed that in the presence of steam (e.g., in the reactions of hydration, steam reforming, etc.) the Lewis acid sites (LAS) on γ-Al_2O_3 can transform to the Bronsted acid sites (BAS). To elusidate the nature of γ-Al_2O_3 acid sites, we studied the adsorption of H_2O and D_2O on γ-Al_2O_3 surface using *in situ* FTIR spectroscopy.

Fig. 1 exemplifies the IR spectra of H_2O adsorbed on γ-Al_2O_3 as a function of temperature. Clearly, as the temperature increases, the intensity of a.b. at 1653 cm^{-1} (δ_{H2O}), corresponding to water adsorbed on LAS (structure I), decreases, whereas that of a.b. in the range of 3670-3770 cm^{-1}, attributed to the terminal and bridging hydroxyl groups (structure II), increases. The attribution of the absorption bands is confirmed by experiments on deuterium-hydrogen exchange on γ-Al_2O_3.

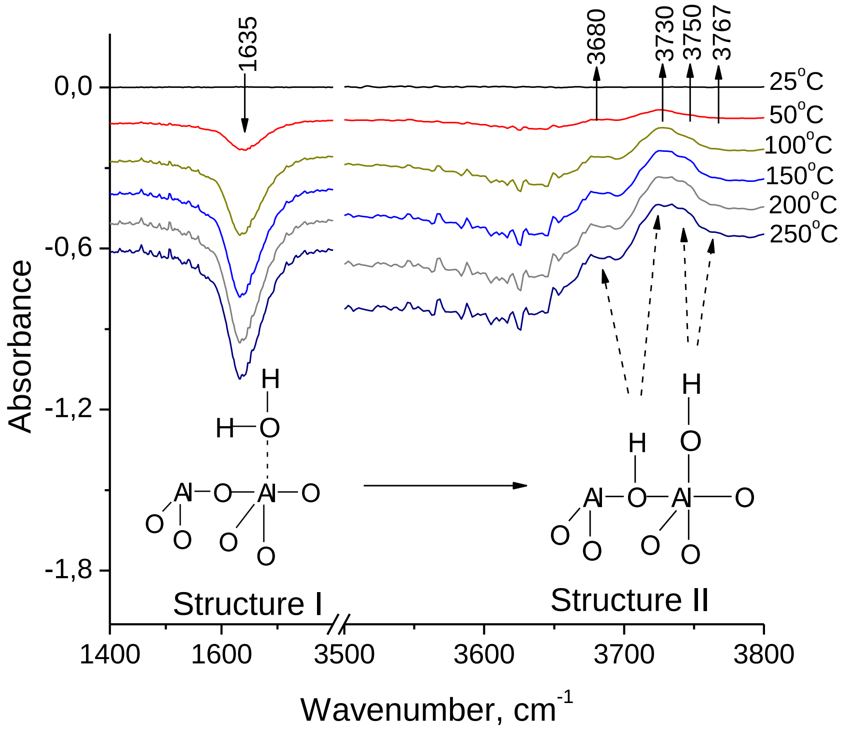

Fig. 1. FTIR spectra of γ-Al_2O_3 after H_2O adsorption

Acknowledgement. This work is conducted within the framework of budget project No. 0303-2016-0011 for Boreskov Institute of Catalysis.

PP-10

Interaction research CO with the surface of the catalyst on the basis of CeO_2 by method of isotope exchange

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In this paper we report our results regarding the isotopic exchange reaction:
$^{12}C^{18}O + {}^{13}C^{16}O \leftrightarrow {}^{12}C^{16}O + {}^{13}C^{18}O$ over CeO_2 catalyst between –162 and +400 °C.

As the catalyst the cerium dioxide received by a deposition from cerium nitrate solution ammonium carbonate solution with after bake and an incideration on air was used. Before the research powder of dioxide of cerium was tableted. The specific surface area measured by the low-temperature adsorption of a krypton made 75 m^2/g. According to the X-ray phase analysis, dioxide of cerium represented cubic modification.

Speed of exchange was counted on the equation of first order:

$$K = -\frac{N}{mS\ t}\ln(1-F) \quad (1)$$

The rate of the isotopic mixing reaction:

$$^{13}C^{16}O(M29) + {}^{12}C^{18}O(M30) \leftrightarrow {}^{13}C^{18}O(M31) + {}^{12}C^{16}O(M28)$$

was followed by continuous measurements of the ratio M(30)/M(31) when an approximately equimolar mixture of $^{12}C^{18}O$ and $^{13}C^{16}O$ was allowed to contact the CeO_2 catalysts. Mass spectrometric measurements of the gases were made with a model MI-1305 spectrum scientific. [1]

The research was conducted with a pressure of 20 mm with the forced circulation of gas. Before studying the CeO_2 was pumped at 400 °C until the pressure was 10^{-6} mm or less. Reaction of isotope exchange was studied in the range of temperatures –162 - +400 °C. In all studied interval of temperatures the exchange kinetics well is described by the equation of first order (1). In an initial instant 1-2 minutes, isotope exchange proceeds with larger speeds which do not manage to be measured, eventually the catalytic activity reaches the steady-state value.

There are two temperature areas of course of exchange differing in activation energy size. In the field of temperatures +25 - +230 °C the speed of exchange goes down with body height of temperature.

The isotopic exchange reaction occurs with an activation energy of 55 kJ/mol in the measured temperature range +230 - +400 °C. In the same temperature range, both CO dissociation and CO disproportionation reactions are absent. This observation supports a nondissociative mechanism for CO isotopic exchange on Ce cations.

The low-temperature exchange proceeds an activation energy of 18 kJ/mol in the measured temperature range –196 - +25 °C. A concerted «four-center» mechanism was proposed for the exchange process.

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PP-11

V(III) Catalyzed Polymerization of α-Olefins: Detailed NMR Spectroscopic Characterization of Intermediates Modeling Active Species of Polymerization

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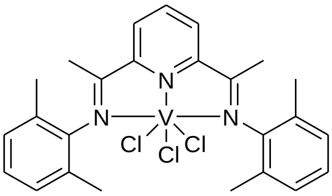
Vanadium catalysts have been used since 1960th for the production of ethylene/propylene co-polymers or ethylene/propylene/diene elastomers (EPM and EPDM rubber). Vanadium based catalyst systems afford polymeric products with unique properties (amorphous, uniform copolymers), which makes them indispensable for the manufacture of synthetic rubber [1, 2]. In spite of the efforts invested in the design of vanadium polymerization catalysts, little is known about the nature of the active species of olefin polymerization.

In this work, ^{1}H, ^{2}H, and ^{19}F NMR spectroscopy was used to study the activation of bis(imino)pyridine vanadium(III) chloride $LVCl_3$ (complex **1**, Scheme 1) with $AlMe_3/[Ph_3C]^+[B(C_6F_5)]_4^-$, $AlMe_2Cl/[Ph_3C]^+[B(C_6F_5)]_4^-$, $AlMe_2Cl$ or MAO co-catalysts in the presence and absence of tetrahydrofurane (THF). The following ion pairs were identified: $[LVCl(\mu\text{-}Cl)_2AlMe_2]^+[A]^-$, $[LVMe(\mu\text{-}Cl)_2AlMe_2]^+[A]^-$, $[LVCl_2(THF)]^+[A]^-$ and $[LVClMe(THF)]^+[A]^-$ ($[A]^- = [AlMe_3Cl]^-$, $[B(C_6F_5)_4]^-$ or $[MeMAO]^-$) (Scheme 1). The nature of the active species of ethylene polymerization by the systems **1**/$AlMe_3/[Ph_3C][B(C_6F_5)_4]$, **1**/$AlMe_2Cl/[Ph_3C][B(C_6F_5)_4]$, **1**/$AlMe_2Cl$, and **1**/MAO is discussed. Catalyst deactivation pathways are also proposed.



Scheme 1. Structure of the complex 1 studied in present work

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (grants № 16-03-00236 and 16-53-53014) and Ministry of Science and Education of the Russian Federation. The NMR measurements and polymerization experiments were performed using the equipment of the Russian Academy of Sciences and the Federal Agency for Scientific Organizations (project 0303-2016-0009).

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NO + H_2 reaction over Pd(110): a detailed mechanism

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Nitrous oxide and ammonia are undesired byproducts in the catalytic reduction of NO with H_2 occurring in automotive catalytic converters. Therefore, it is necessary to improve the selectivity to N_2 in this process. Also it seems to be useful the detailed studying of product formation routes for developing fundamental aspects in the field of catalysis by platinum metals. In this work, we present a detailed study of the mechanism of nitric oxide reduction with hydrogen on the Pd(110) that provides a diverse set of active centers for adsorption.

Temperature-programming desorption (TPD) and temperature-programmed reaction (TPR) data shows that the reaction occurs in the regime of surface explosion, the rate-limiting step is a NO_{ads} dissociation into highly reactive O_{ads} and N_{ads} atoms. The steady-state NO + H_2 reaction leads to formation of the products: N_2, H_2O, NH_3 and N_2O. Observed hysteresis phenomena in the H_2O and NH_3 formation rate during a heating-cooling cycle is probably due to NO accumulation at low temperatures followed by surface explosion at T ~ 495 K.

Binding energies and structural parameters of species involved in the NO + H_2 reaction over Pd(110) adsorbed at possible sites have been calculated using the QUANTUM-ESPRESSO package based on Density Functional theory. The reaction routes of NO dissociation and of the possible products formation were considered by the Climbing Image Nudge Elastic band Method (CI-NEB).

The rate-limiting role of NO dissociation was confirmed by the calculations. It was first detected moleculary adsorbed on Pd(110) hydrogen with E_{ads} of -0.34 eV and E_{diss} of 0.31 eV. It was found that N_2 formation occurs via recombination of two nitrogen atoms co-adsorbed in the same valley between rows of the Pd(110). N_2O can be formed from the combination of the NO molecule with the N produced during the NO dissociation on the surface: $NO_{ads} + N_{ads} \rightarrow N_2O_{ads}$. The mechanism of NH_3 generation involves the consecutive addition of hydrogen atoms to the nitrogen atom formed by the dissociation of NO_{ads} and the highest energy barrier corresponds to the first step so the formation of NH_{ads} intermediate is the rate-determining step for the NH_3 formation. It was demonstrated that OH_{ads}-group formation is rate-limiting step of water molecule generation. Subsequent H_2O formation occurs via two pathways: $OH_{ads} + H_{ads} \rightarrow H_2O_{ads}$ and $OH_{ads} + OH_{ads} \rightarrow H_2O_{ads} + O_{ads}$. The disproportionation reaction of OH intermediate is preferred.

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PP-13

Self-condensation of Pentanol over VIII Group Metals: Role of Active Sites

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Alcohols are an important class of organic compounds because of their wide-spread application in laboratory and industrial practice [1,2]. Due to increasing availability of bio-based alcohol feedstock and a quest for synthetic biofuels and biochemical, a promising route to convert valeric acid derived 1-pentanol [3] into branched heavier 2-propylheptanol (Guerbet alcohol) was studied in the current work (Fig. 1).

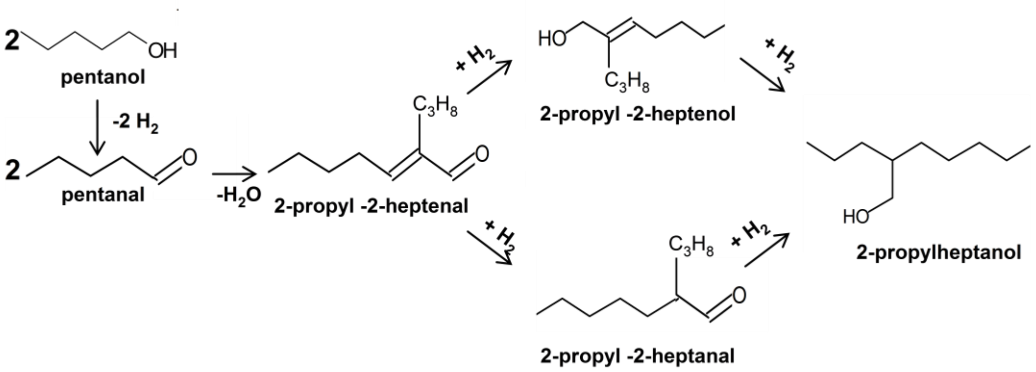

Fig. 1. Scheme of pentanol-1 self-condensation

This reaction was carried out in a batch mode from 140 to 200 °C, under N_2 (1-10 bar) in the presence of VIII group metals and a base – NaOH. It was shown that pentanol condensation mainly resulted in formation of the target product 2-propylheptanol whereas pentanal, 2-propyl-2-heptenal, 2-propyl-1-heptanal, 2-propyl-1-heptenol were observed in minor quantities. The effect of noble metals as catalysts and reaction conditions on 1-pentanol conversion and selectivity to 2-propylheptanol was studied. Conversion of pentanol increased in the order $Ir/CeO_2 \ll Rh/Al_2O_3 < Pd/ZrO_2 < Ru/C < Ir/C < Pd/C < Pt/C < Pt/Al_2O_3$. Selectivity to 2-propylheptanol was increased in the sequence $Ir/CeO_2 \ll Ir/C < Ru/C < Rh/Al_2O_3 \sim Pd/C \sim Pt/C \sim Pd/ZrO_2 \sim Pt/Al_2O_3$ being substantially influenced by temperature. Pd/C, Pt/C and Pt/Al_2O_3 catalysts were shown to demonstrate the highest yield of 2-propylheptanol. In addition, interactions of the alcohol with the alkali modified Pt/Al_2O_3 catalyst was investigated by UV–vis and FTIR spectroscopy to elucidate the role of catalytic active sites involved in alcohol self-condensation reaction mechanism.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-03-09329. Part related to catalyst synthesis was supported by Russian Academy of Science Project No.V.47.1.12.

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PP-14

Transformation of C5 Acid Catalyzed by Supported Ir in H_2: Size Effect

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Recent developments in catalytic reduction of carboxylic acids using molecular hydrogen related to the field of biomass up-conversion have exploited catalysts based on noble metals [1]. Herein, supported Ir catalysts optimized by Re over different metal oxide supports, are reported for the selective conversion of levulinic acid derived pentanoic acid (PA) to pentanol and further to C5 alkanes.

Liquid phase PA hydrogenation in decane as a solvent (180 °C, 25 bar) was studied over Ir and IrRe catalysts supported on alumina, ceria and zirconia. Before catalytic test all catalysts were preliminary treated in H_2 at 415 °C during 5 h. The reaction products were analyzed by "Chromos 1000" GC (FID) with Stabilwax-DA column (50 m/0.32 mm/0.5 µm) (USA) at 373-473 K with ramp 10 K/min. Catalysts were characterized by H_2 TPR, XRD, XPS and HRTEM. XPS study revealed metallic state for Ir in studied catalysts while Re was partially oxidized (XPS and XRD). A series of the most active IrRe/Al_2O_3 was prepared varying Ir particle size from 0.8 to 3.2 nm as verified by TEM (Table).

Table. Effect of Ir particle size (d_s) on PA conversion and selectivity to 1-pentanol (Reaction conditions: PA 0.875 mmol, decane 25 mL, IrRe/Al_2O_3 480 mg, 180 °C, P(H_2) 2.5 MPa

	d_s, nm	PA conversion, %		Selectivity to pentanol, %	
		after 0.5 h	after 1.5 h	after 0.5 h	after 1.5 h
1	0.8	15.5	37.4	90.8	91.1
2	1.0	18.1	38.1	91.0	91.3
3	1.7	47.1	84.0	93.0	93.3
4	3.2	54.2	99.4	94.6	92.1

It was found that both PA conversion and a little bit selectivity to pentanol increased with an increase of mean Ir particle size. Similarly, on the basis of catalytic and spectroscopic characterization results, large Ru particles were established as the preferred active sites for stearic acid conversion [2]. Doping of Ir with Re gave a rise of PA conversion and selectivity to pentanol in the absence of by-side decarboxylation reaction. Conversion of pentanoic acid increased in the order Ir/CeO_2 < Ir/ZrO_2 < IrRe/ZrO_2 < IrRe/Al_2O_3. Selectivity to pentanol increased in the sequence Ir/Al_2O_3 < Ir/CeO_2 ~ Ir/ZrO_2 < IrRe/ZrO_2 < IrRe/Al_2O_3 [3].

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-03-09329.

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PP-15

Synthesis, structure and stability of $Rh_xCe_{1-x}O_{2-\delta}$ solid solution – a model catalyst for CO oxidation

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Rhodium is one of the noble metal used in tree-way catalysts for neutralization of exhaust gases. For tree-way catalysts, CeO_2 is used as promoter due to oxygen storage properties. According to the literature in Rh-CeO_2 system ion rhodium is formed on the surface of ceria, which plays important role in many oxidation reactions. Many researchers point out that catalytic activity enhance when $Rh_xCe_{1-x}O_{2-\delta}$ solid solution is formed. However, the structure and properties of Rh-CeO_2 solid solution has not been studied yet. Therefore, the aim of this work is detailed analysis of structure and stability of Rh-CeO_2 solid solution with different Rh loading.

Five series of catalysts with rhodium loading of 1, 5, 8, 13 and 17 % wt were prepared by coprecipitation method. This method allows obtaining samples with a wide range of Rh content in a solid solution. Samples were synthesized from solutions of rhodium and cerium nitrate, followed by calcination at various temperatures ranging from 450 to 1000 °C. All samples were studied using set of methods: XRD and XPS. The local structure of Rh-CeO_2 solid solution was analyzed by Pair Distribution function (PDF) method. The diffraction data for the PDF were obtained using synchrotron radiation at station ID21 (Grenoble, France) of the ESRF. $\lambda = 0.177$ Å.

The XRD data indicate that samples with rhodium loading 1-8 % wt are single fluorite phase at calcination temperature below 1000 °C. The lattice parameter of the fluorite phase decreases with increase of Rh loading. Samples with rhodium loading 13-17 % wt have additional amorphous phase. According to XPS data, the rhodium state in all samples is Rh^{3+}. It can be attributed to rhodium in $Rh_xCe_{1-x}O_{2-\delta}$ solid solution. At calcination temperature 1000 °C the additional phases Rh_2O_3 and $Ce_{0,56}Rh_2O_4$ are observed.

According to PDF data $Rh_xCe_{1-x}O_{2-\delta}$ solid solution exhibit the fluorite structure on local level for samples with rhodium loading 1-8 % wt, additional peaks were not detected. Ion Rh^{3+} with octahedral coordination replaces Ce and don't generate new distances. Intensity of the main fluorite-type distances decreased and some additional peaks were detected for samples with rhodium loading 13-17 % wt. We attribute these additional PDF peaks to distances in Rh_2O_3 and/or $Ce_{0,56}Rh_2O_4$ amorphous phases.

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PP-16

Preparation and Study of Iron Oxide/Inorganic Matrix of Oil-Bearing Rocks Catalytic Systems for Enhanced Oil Recovery

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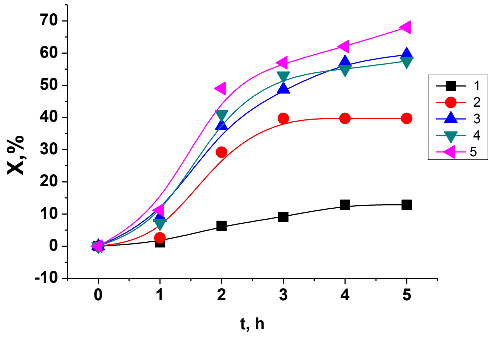
In this work, the synthesis and catalytic activity measurements of the active systems based on iron oxide/natural matrix (basalt, clays, sandstone) for methane oxidation, decomposition of ammonium nitrate and hydrocracking of asphaltenes as models for in-situ catalytic stimulating oil recovery are presented. Catalytic systems were prepared by a hydrothermal synthesis at T = 433-473 K and pressures of 0.6-1.6 MPa via joint hydrolysis of urea and ferric (III) chloride. Microstructure and morphology of catalysts were investigated by X-ray diffraction, thermo gravimetric (TG), transmission electron microscopy (TEM) and nitrogen (N_2) adsorption-desorption isotherms. According to the XRD data, the single phase of iron oxide - hematite (α-Fe_2O_3 JCPDS 13-534) is formed in all kinds of matrices as a result of hydrothermal hydrolysis of iron chloride at temperatures of 453 K and 473 K, while akagenit and goethite-iron oxyhydroxides (respectively: β-FeOOH, JCPDS 13-157 and α-FeOOH, JCPDS 29-713) have been found at lower temperatures. Catalyst systems used in model reactions are presented a hematite having a particle size D = 11.0 nm (prepared at 453 K) and 20 nm (synthesized at 473 K) fixed on the matrices.

The experimental data on the intrinsic activities of matrix samples and on the activities of supported Fe_2O_3/matrix catalysts have confirmed the possibility to use the natural properties of matrices to create advanced catalytic processes of intensification of oil production. The methods developed for the preparation of catalysts and a method for introducing precursors into matrix may be used in a possible application in oil fields.



Ammonium nitrate conversion in the presence of Fe_2O_3/matrix systems and Pt/Al_2O_3 catalyst

(the ratio $HNO_3 : HCOOH : NH_4NO_3 = 7.8 : 3.4 : 1$, $HNO_3 : HCOOH = 2.3$, T = 324 K)

1 – blanc experiment, 2 – commercial catalyst 0.56 Pt / γ-Al_2O_3, 3 – 1.2 % Fe /sand matrix, 4 – 11.4 % Fe/clay matrix, 5 – 12.5 % Fe_2O_3/basalt matrix

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PP-17

Synthesis and photocatalytic properties of anodized titania nanotubes

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Titania is inert under visible light for use in photocatalysis. Reducing its energy gap eliminate this disadvantage. In this regard, the aim of the work was a synthesis of an active under visible light photocatalyst based on the nanotubular non-stoichiometric TiO_2 film.

Anodizing was carried out on the Digma installation, consisting of a power source, an electrochemical cell and a thermostat. A titanium foil 100 μm thick was pretreated in acetone and aqueous acid mixture at a volume ratio of HNO_3:HF:H_2O = 6:1:18. Primary anodizing was carried out at a constant voltage (U = 20 V) in the NH_4F + ethylene glycol, 1 wt.% solution for 10 min at a temperature of 20 °C. The resulting oxide layer was removed in the acid mixture HNO_3:HF:H_2O=1:1:20 for 3 min for aligning titanium surface. The secondary anodizing was performed under the same conditions with varying oxidation time between 15 and 360 min. All materials used in the chemical reagents were pure for analysis qualifications.

Analysis of resulting structure showed that with increasing time of anodization from 15 to 360 min nanotube length initially increases to about 2 μm, and then starts decreasing, their inner diameter is increased to 39 nm, and the effective cross-sectional area of nanotubes increases to 415 cm^2 of the 2 cm^2 film diameter. The XRD pattern of the samples had approved the amorphous atomic structure of the nanotubes. Diffuse reflectance spectra and Kubelka-Munk formula allowed to calculate the energy gap of E_g = 3.35 eV.

Photocatalytic activity was measured in a flow reactor, the reactants with the detection reaction by FTIR spectrometer. Illumination was done with LED of 450 nm maximum emission light wavelength, and the power supply current of 1.0 A / 30 V. Other conditions were as follows: acetone concentration of 800 ppm, relative humidity 20 %, T = 40 °C, flow rate 60 ml/min. The acetone concentration in the range of 1160-1265 cm^{-1}, carbon dioxide concentration – 2200-2450 cm^{-1}. The photocatalytic oxidation rate was calculated from the accumulation of carbon dioxide, the only gaseous product of the acetone oxidation.

The catalytic activity of the three different TiO_2 films, synthesized under the same conditions for 120 min at the length of nanotubes 1, 1.5, and 2 μm ranges widely from 2.9 to 5.2 nmol/(min·mg), indicating a significant role nonstoichiometry and morphology of the synthesised films. Thus, the maximum of photocatalytic efficiency is shown in a 2 μm nanotubes sample. These results indicating the prospects of using the nanotubular TiO_2 with the synthesis procedure described in present work.

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PP-18

The oxidative conversion of methane

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Oxidative conversion of natural gas in a motor fuel component in the raw material for petrochemistry and organic synthesis over many decades is the subject of intense research are driven by the problem of reducing the hydrocarbon resources of petroleum origin. Of particular interest in this respect are the processes of oxidative conversion of methane to synthesis gas and oxidative dimerization of methane to C_2-olefins. For countries with large reserves of cheap natural gas, the practical implementation of these processes today seems economically justified. Therefore, the creation of highly efficient, selective and stable catalysts for processing light hydrocarbons to produce valuable products of petrochemical synthesis is an important practical and strategic objective.

We report here on the activity of oxide catalysts (low percent oxide NiMo / Al_2O_3 composites) in the oxidative conversion of methane to synthesis gas. The NiMo / Al_2O_3 catalysts were prepared by "solution combustion" method. As oxidizers have been used CO_2 (dry reforming), O_2 (partial oxidation) and H_2O (steam reforming). The oxidation of methane was performed separately with oxygen, carbon monoxide and water vapor, and its mixtures (CH_4:O_2: CO_2: H_2O – tri-reforming of methane). Testing the activity of the catalysts developed has been studied at flow regime by varying the composition of the mixture, the space velocity and the process temperature.

It determined that varying the components (CH_4: O_2: CO_2: H_2O) in the reaction gas mixture at the reaction temperature of 750 °C allows to change the ratio of H_2 / CO in the resulting synthesis gas in the range from 1.2 to 3, allowing its using in various syntheses. Synthesized NiMo / γ-Al_2O_3 catalyst is active as in separate reactions (partial oxidation, steam methane conversion and dry reforming) as in the tri - reforming of methane. At the conditions studied methane conversion equal to 82-89 %, concentration of H_2 - 56 %, CO - 38 %. Long-term test of NiMo / γ-Al_2O_3catalyst in the process of tri-reforming of methane showed that over the catalyst is not observed carbon formation. The figure shows photographs NiMo / Al_2O_3 catalyst tested for 20 hours in different processes.


Fresh catalyst


Partial oxidation of CH_4


Dry reforming of CH_4


Tri-reforming of CH_4

Thus, one of the essential advantages of the process tri – reforming of methane is the production of synthesis gas with the desired ratio of H_2 / CO and exclude of carbon formation in the process.

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PP-19

Conversion of bioethanol to valuable products

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Bioethanol from biomass is a renewable source to produce valuable chemical products. The valuable products as ethylene, aromatic hydrocarbons, syn-gas, hydrogen and other products may be prepared by catalytic method from bioethanol [1].

This paper presents the results of producing ethylene and aromatic hydrocarbons from bioethanol. As the catalyst for producing ethylene used cerium containing catalyst supported on zeolite 5A [2]. For the synthesis of aromatic hydrocarbons from bioethanol was studied catalysts based on zinc oxide supported on 3A [3]. The catalysts were prepared by solution combustion method. Experiments to test the efficiency of the catalysts were carried out using an automated flow catalytic device. The reaction was performed at atmospheric pressure and the temperature range of 200-400 °C, W= 30-60 hr^{-1}.

The results showed, that for synthesis of aromatic hydrocarbons the most active is 2 % $ZnOP_2O_5$/КА. At 350 °C and space velocity 60 hr^{-1} the yield of aromatic hydrocarbons is 25 vol. %.

The optimal technological conditions were determined for producing ethylene from bioethanol. Over the 0.5 mas. % Ce_2O_3/5A catalyst at reaction temperature 350 °C and W = 60 hr^{-1} the yield of ethylene is 89 vol. %.

Thus, by varying the catalyst preparation method, its composition, carriers, modifying agents, the technological conditions of the reaction the process may be carried out in a predetermined direction, creating conditions for the synthesis of the title product.

Acknowledgements. This work was supported by the Kazakhstan Ministry of Education and Science**.**

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PP-20

Controlling nanostructure of bimetallic Pd-M (M = Au, Ir, Pt, Ru) catalysts prepared by the reverse "water-in-oil" microemulsion method

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The carbon (Vulcan XC 72) and silica (Davisil) supported 2wt% Pd100-x Mx catalysts M = Au, Ir, Pt, Ru of various Pd/M ratios (Pd90M10 - Pd30M70) were synthesized through a reverse "water-in-oil" microemulsion method (Triton X-114, cyclohexane, $NaBH_4$) at high 0.2 or low 0.02 mol/dm^3 metal precursors concentrations. The catalysts were characterized by XRD, XRF, XPS, SEM-EDS, TEM-STEM, HRTEM. The catalytic hydrogenation of cinnamaldehyde (CAL) was carried out at mild conditions (20-50 °C, 1 atm H_2, toluene). In all catalysts metal particles with a narrow size distribution are very well distributed on surface of carbon and silica supports. Pd-M particles retained (fcc) crystalline Pd structure assisted by a increase in the lattice parameter as the M content grows [1]. The average size of Pd90M10 particles with low M content was similar 5.5-6.0 nm regardless of metal type (Au, Pt, Ir, Ru) vs 6.7 nm for Pd. At higher M content (Pd30Au70) larger particles 7-8 nm in size appeared. The 10-times lower precursors concentration produced slightly smaller Pd-M particles (5 nm vs 6 nm) while all other relations were preserved. The results of CAL hydrogenation showed that the rate of CAL hydrogenation and especially the C=C/C=O selectivity were dependent on the type of M component and nominal Pd/M ratio. On Pd-Au/C remarkable C=O selectivity growth when Au content exceeded that of Pd. The selectivity of Pd90Ir10 and Pd90Pt10 was similar to that for pure Ir and Pt preferring the C=O hydrogenation, while other two Pd90Au10 and Pd90Ru10 catalysts displayed reactivity typical for pure Pd i.e. promotion of C=C hydrogenation. At the same nominal Pd/M ratio, the type of M component affected the nanostructure/surface architecture of bimetallic particles. In electrochemical studies, H-desorption/adsorption peaks and the peaks of the Pd surface oxide formation/reduction on cyclic voltammetry (CV) curves were analysed. A shape and a shift of the peak potential vs pure Pd and the charges referred to the Pd/M mass were determined. The difference of Pd and M reduction potentials and concentration of metal precursors in solution are the key factors determining the degree of Pd/M metal segregation (alloy, core-shell) and surface Pd/M ratio.

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PP-21

Carbon-Supported Active Component as a Type of a Model Catalyst for Soot Oxidation in Automotive Exhaust Particulate Filters

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Intro. Since 1990's, catalytic combustion of soot is of great interest mainly due to strong demand for solutions to decrease vehicular exhaust soot emissions [1]. Catalysts were implemented to lower the temperature of diesel particulate filters (DPF) regeneration [2].

Standard method of kinetic studies of soot combustion consists in burning mixture of soot and catalyst in the TPO ramp measuring rate of CO_X evolution or C disappearance. Contact condition between catalyst and soot is very important. Uncertainty in the definitions of often used "loose" and "tight" conditions cause difficulties in comparing and implementing results. Another important parameter is soot-to-catalyst mass ratio (SCMR). In most cases, SCMR used in the lab experiments is 1/20 to 1/5, being much lower than the real SCMR within DPF.

The aim of the work is to evaluate a concept of the model catalyst for soot oxidation characterised with (i) "extra-tight" catalyst-soot contact, (ii) realistic ratio between catalyst and soot. Such model catalyst represents intrinsic activity of the component towards soot oxidation.

Experimental. Samples with "extra-tight" catalyst-soot contact condition were prepared according to [3]. Activated carbon (AC) was impregnated with solution of the Pt pre-cursor, followed by drying and reduction. SCMR directly corresponds to the Pt loading of the sample. SCMR of 17/1 (6 % wt. Pt on AC) was investigated. Pure support material (AC) was characterized as well as a reference sample.

Samples were characterized for a reactivity in $C+O_2$ reaction using TPO in O_2-He flow, with CO_2 and O_2 measured with MS. PGM sites availability, PGM particles size were characterized with flow chemisorption methods.

Results. For the sample 6 % Pt-AC representing proposed by the authors new type of the model catalyst for studying soot oxidation, i.e. with extra-tight catalyst-soot contact condition and realistic SCMR, the following soot combustion characteristics were measured in TPO run in dry O_2-He mixture: $T_{10\%/50\%/90\%}$ ~ 400 °C/493 °C/575 °C. The low-temperature shift vs. reference sample was: $\Delta T_{10\%/50\%/90\%}$ ~ 210 °C/193 °C/217 °C. Main kinetic parameters were obtained by fitting a simplified kinetic model to experimental data.

Conclusion. New type of the model catalyst for soot oxidation, with extra-tight catalyst-soot contact condition and realistic soot-to-catalyst mass ratio, allows measuring real potential of the given catalyst, including correct comparison of different catalysts and using intrinsic kinetic parameters directly in different soot combustion/DPF regeneration models.

Acknowledgement. Thanks to NSU for borrowing ChemBET Pulsar TPR/TPD and Cirrus 2 to us.

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On the "Chemisorption" Particle Size Measurements for PGM/C Low-Temperature CO Oxidation Catalysts

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Chemisorption methods are widely used for the characterization of the active sites of heterogeneous catalysts. So-called "chemisorption" particle size can differ from the particle size determined by TEM and XRD [1]. For a catalyst, the characteristic of the active sites based on adsorption/reaction behavior may look more important, than a real size of the metal particle.

In this work, "chemisorption" particle size of the active metal for specific class of supported catalysts is discussed. The objects of the study are PGM supported on a carbonaceous material: (1) Pd/C-fiber; (2) Pt/Activated Carbon, both representing low-temperature oxidation catalysts.

The catalysts Pd/C-fiber were prepared as described in [2]. Pt/AC catalyst was prepared by the method [3]. "Chemisorption" particle size was estimated by CO pulse chemisorption. By default, a sample of catalyst (~25-200 mg) in a U-reactor, was dried in He flow 10 min@140 °C, reduced in H_2 flow 1h@300 °C, purged in He flow 1h@300 °C, cooled in He flow to 35 °C. Titration of active sites were performed with pulses of 10 vol. % CO-He at a sample temperature of ~35 °C. Titration was carried out using ChemBET Pulsar (Quantachrome).

PGM dispersion/particle size measured for the samples after “default” treatment, is given in Table 1. By applying oxidative pretreatments, catalysts can be "improved" (Table 1).

Table 1. Dispersion (%) / Chemisorption effetive particle size (D avg, Å) of the active metal

Pretreatment/Sample	**Pd/CF #1767**	**Pd/CF #1780**	**Pt/AC KL-79**
Default	5.7%/200Å	5.1%/220Å	9.7%/117Å
O2 5 min@150 °C	11.4%/98Å	12.5%/90Å	12.9%/88Å
O2 5 min@200 °C	11.9%/94Å	16.1%/69Å	12.9%/88Å
O2 5 min@250 °C	n.m.	n.m.	13.0%/87Å

The higher temperature of the oxidative pretreatment, the higher measured PGM dispersion is observed, displaying saturation. A similar effect was observed for PGM/carbon catalysts in [1]. The observed results suggest that in the initial catalysts a substantial fraction of the metal particles’ surface is screened by the carbon matrix. Oxidative treatment leads to catalytic oxidation of carbon on the PGM particle/Carbon interface (confirmed by CO_x evolution recorded with MS). After oxidation of all the carbon being in direct contact with the PGM particles, active metal particles have maximum performance in accordance with their real size.

The method described can be used to activate any of the catalysts “PGM/C-support”.

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Compositional Changes of the LNT Catalyst Caused by Aging: Statistical Analysis of the XPS/Ar$^+$-Etching Data

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Automotive applications of diesel NOx storage/ reduction catalysts (LNT) face problems coming from the catalysts deactivation. Present work was set up to correlate the main compositional changes of the sub-surface layer of the LNT with aging process parameters.

For the aging, cores of 1”D x 6”L cut from diesel monolith LNT catalyst of 5.66”D x 6”L were used. These samples were treated in multiple sulfation-desulfation (DS) cycles using Ford prototype diesel engine operating with realistic LNT protocol. The cores were taken out after 1, 10 and 100 DS cycles in sulfated and desulfated state. Then, the cores were cut into 3 specimens representing inlet, middle and outlet location within the catalyst brick.

The in-depth profiles of the main components were measured with help of Ar+-ion etching coupled with XPS, the procedure is described in details elsewhere [1]. Resulted data set was modified and statistically processed using Ford Minitab™ software.

The initial data-set contained 85 data points (X/Al atomic ratios measured by XPS for 10 components - Ba, Ce, Zr, Pt, Pd, Rh, Ca, P, Zn, S), measured vs. given number of the DS Cycles, catalyst status (Sulfated and Desulfated), axial location, and depth into the catalyst. Then, factor analysis (FA) was performed respecting main basic rules of the FA.

As the result of the FA, 14 initial variables were split into 5 main factors that behaved closely to independent variables. Now, inside each factor, statistically true correlations between variables can be observed and interpreted vs. parameters of aging procedure.

Based on the performed statistical analysis of the XPS/Ar+-etching results, the following main aging-related LNT sub-surface layer compositional changes were suggested:

1. Contaminating sub-surface layer of the catalyst with oil-derived elements (P, Zn, Ca) - could lead to poisoning/blocking active sites, including Ce phosphate formation [2]
2. Redistributing Ba and Ce within the sub-surface catalyst layer during aging (enrichment with Ba, depletion with Ce) might be caused by interactions of Ba and Ce with NOx and SOx, leading to dis-balance of the NO oxidation and NOx storage/reduction functions.
3. Decreasing measured Pt content along the axial direction, possibly due to Pt sintering caused by high temperatures observed in the catalyst brick during desulfation.
4. Accumulation of S along the aging, indicating about incomplete desulfation and leading to taking fraction of Ba sites off from the NOx storage process.

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PP-24

Selective oxidation of butenes with nitrous oxide

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In the last decades, nitrous oxide (N_2O) has attracted growing attention as a selective oxidant for both catalytic and non-catalytic oxidation of various hydrocarbons into valuable oxygenates [1, 2]. In this work, a new method for obtaining C2-C4 carbonyl compounds via a selective gas-phase oxidation of butane-butylene fraction (BBF) with N_2O is reported.

The industrial BBF used contained 32.9 % 1-butene, 39.4 % 2-butene, 15.1 % isobutene, 1.6 % isobutane, and 10.5 % n-butane. The reaction with N_2O was carried out without a catalyst in a flow reactor (25 cm^3) at 350-500 °C and a pressure of 5-20 atm (Table 1). The reaction mixture included 10-30 vol.% N_2O and 90-70 vol.% BBF. The flow rate was 25 cm^3/min. Under these conditions the butenes in the composition of BBF are oxidized by N_2O yielding a mixture of carbonyl products containing acetaldehyde (12-18.7 %), propanal (13-16 %), methyl ethyl ketone (45-50 %), acetone (12-14 %), butanal (2.4 %) and isobutanal (3-5 %). Additionally, C5 derivatives of cyclopropane are formed (3-9 %)

For example, for the reaction mixture containing 30 % N_2O and 70% BBF, the N_2O conversion at 450 °C and a pressure of 10 atm is 78 %, the total conversion of butenes is 40.5 % (run 6, Table 1). The total selectivity to carbonyl products (S_{CO}) is 90 %, the selectivity to methyl ethyl ketone is 43.6 %, and the selectivity to cyclopropane derivatives (S_{C5}) is ~6 %. In this case, the total productivity for carbonyl products (Pr) reaches 9.9 mmol/l·min (37.5 g/l·hr), which is comparable with the productivity of some commercial chemical processes.

Table 1. Gas-phase oxidation of butane-butylene fraction (BBF) with N_2O

№	P, atm	T, °C	X_{N2O}, %	X_{but}, %	S_{CO}, %	S_{C5}, %	Pr, mmol/l·min
Reaction mixture: 10% N_2O, 90% BBF							
1	5	500	100.0	13.6	88.5	8.7	4.2
2	10	450	95.0	12.8	89.0	2.8	4.0
3	20	350	37.5	5.2	93.2	4.5	1.7
4		400	87.0	11.9	89.4	5.5	3.7
Reaction mixture: 30% N_2O, 70% BBF							
5	10	400	31.0	17.1	92.0	5.6	4.3
6		450	78.0	40.5	90.0	5.9	9.9

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PP-25

Effect of olefins structure on their selective oxidation with nitrous oxide

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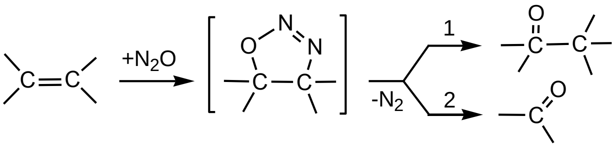
The development of efficient and environmentally acceptable methods for producing ketones and aldehydes remains one of the most challenging problems. Recently it was shown that the thermal liquid phase oxidation of olefins with nitrous oxide (N_2O) at 200-280 °C yields carbonyl compounds with a high selectivity often exceeding 90 % [1]. This opens a new synthetic way to valuable oxygenated products. The possibility of industrial use of the method was shown by BASF. The reaction proceeds by 1,3-dipolar cycloaddition mechanism via [1,2,3]-oxadiazole intermediate. Main route 1 of the reaction leads to ketone or aldehyde:



Depending on the orientation of N_2O molecule during cycloaddition to the C=C bond, different reaction pathways are possible. The reaction can also proceed with cleavage of the C=C bond (route 2). In this work, the effect of olefins structure on their reactivity towards N_2O and the ratio of the reaction routes were studied.

It was found that the oxygen atom of N_2O attaches preferably to the second carbon atom of terminal olefins. For terminal monosubstituted olefins ($RCH=CH_2$) a contribution of this route to the total oxidation rate is 70 % for propylene, 79-83 % for 1-butene, 1-hexene, and 1-octene [2]. In the case of isobutene $(CH_3)_2C=CH_2$ with 1,1-disubstituted C=C bond the contribution of this route reaches 90 %. The contribution of the cleavage route (F_{cleav}) also depends on the olefin structure. In the case of internal 1,2-disubstituted olefins ($R^1CH=CHR^2$, e.g. 3-heptene), the F_{cleav} value is relatively low: ~4 % for cis- isomer and ~14 % for trans-isomer [3]. The oxidation of such olefins leads mainly to ketones. For terminal monosubstituted olefins ($RCH=CH_2$), the F_{cleav} value increases to ~30-40 %, and their oxidation yields a mixture of ketones and aldehydes. For internal trisubstituted olefins ($R^1R^2CH=CHR^3$), for example, 2-methyl-2-pentene, the F_{cleav} is ~ 30 %. In the case of olefins with 1,1-disubstituted C=C bond ($R^1R^2CH=CH_2$) the cleavage route becomes dominant: e.g. for isobutene the F_{cleav} value is ~90 %. The olefin structure also affects its reactivity towards N_2O. The reactivity decreases in the order 1-butene > 2-buten > isobutene. At the same time, cis- and trans- isomers of 1,2-disubstituted olefins have similar reactivity.

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PP-26

Palladium catalysts for nitrobenzene hydrogenation

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The catalytic activity of bimetallic Pd-Cu, Pd-Ag, and Pd-Ni catalysts in the reaction of nitrobenzene hydrogenation was studied. The reaction of nitrobenzene hydrogenation was carried out in a batch system at a constant (normal) pressure and a temperature of 60 °C. The bimetallic catalysts were prepared by the reduction of the solutions of a palladium salt and other metal salts with hydrazine. Four preparation procedures, which differed in the orders of the introduction and reduction of the reagents, were tested for each particular bimetallic pair. The palladium content of all of the bimetallic catalysts was 4 %.

We found experimentally that the majority of the test bimetallic catalysts possess higher catalytic activity than that of palladium metal. Note that the nature of the second metal has an essential effect on the catalytic properties of palladium. The catalytic activity of the bimetallic systems increased in the order Pd-Cu<Pd-Ag<<Pd-Ni. The catalytic activity of the Pd-Ni system is higher than that of other systems (Pd-Cu and Pd-Ag) by a factor of 3-17.

The effects of the second metal and other promoters on the efficiency of catalysts in the hydrogenation reaction are related to their influence on the geometric and/or electronic properties of the active centers of the catalyst. In our opinion, this is due to the electronic interaction of the atoms of palladium and the second metal. We assumed that the catalyst preparation procedure can also have a strong effect on catalytic activity.

The influence of the carrier nature on the efficiency of palladium catalysts was studied also. We found that the matrix nature did not have a significant effect on the catalytic activity when the palladium content was 4 %. This is due to the fact that with increasing specific surface in the range from the zirconium oxide to aluminum oxide in 27.4 times the reaction rate increases 1.3 times

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PP-27

Heterogeneous catalysts based on divanadium-substituted polyoxotungstate in liquid-phase oxidation of 2,3,6-trimethylphenol with hydrogen peroxide

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The selective oxidation of aromatic rings of alkylarenes with atom efficient and green oxidants, e.g. H_2O_2, is a challenging goal. Aromatic oxidation of alkylbenzenes [1,2] and alkylphenols [3] can be efficiently catalyzed by a divanadium-substituted polyoxometalate (V_2-POM), $TBA_4[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OH)]$. In this work, we explored immobilization of V_2-POM on various solid supports (SiO_2, amine-modified SiO_2, metal-organic framework MIL-101, active carbon Sibunit, and carbon nanomaterials [4]) and evaluated catalytic performance of resulting solid catalysts in the industrially relevant oxidation of 2,3,6-trimethylphenol (TMP) with aqueous H_2O_2.

The most promising results were obtained for V_2-POM supported on carbon nanomaterials, in particular, nitrogen-doped carbon nanotubes (N-CNTs). Several catalyst samples have been prepared using N-CNTs with 6 wt.% of N, varying the content of V_2-POM in the range of 5-25 wt.%. The optimal amount of V_2-POM proved to be around 15 wt.%. The catalyst showed excellent TMP conversion (98 %) and selectivity (98 %) towards 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, Vitamin E precursor). Only 90 % selectivity was attained over 5%V_2-POM/6%N-CNTs. Decrease in the nitrogen content in N-CNTs also resulted in lower selectivity (85-90 %). The critical factor that strongly affects both adsorption of V_2-POM and catalytic performance of the immobilized POM turned out wetness of N-CNTs. High water content in the support leads to decrease in the attainable V_2-POM loading and, moreover, impairs selectivity of the resulting catalyst even if it contains the optimal amount of the POM. Studies by TEM revealed a uniform molecular distribution of V_2-POM over the support. FT-IR spectroscopy confirmed the retention of the V_2-POM structure after immobilization and catalytic reaction. XPS indicated that the N-CNT support is stable to oxidation under the conditions employed. Hot filtration tests proved truly heterogeneous nature of the oxidation catalysis. The catalyst can be easily separated from the reaction mixture by filtration, regenerated by evacuation and used repeatedly without deterioration of the catalytic performance during several recycles.

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New Method of Solving the Inverse Problem of Chemical Kinetics for Catalytic Reactions

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The problem of determining unknown kinetic parameters from unsteady-state experimental data is among the most complicated problems of chemical kinetics: it involves uncertainties and may have multiple solutions. We developed a method of determining the rate constants of elementary steps for catalytic reactions whose every step involves at least one main reactant. Consider, in general form, a catalytic reaction that involves the main reactants ($\mathbf{A}_k$) and intermediates (X_j) and consists of the elementary steps

$$\sum b_{ik}\,\mathbf{A}_k + \sum a_{ij}\,X_j = \sum a_{-ij}\,X_j + \sum b_{-ik}\,\mathbf{A}_k\,,\ i=1,\ldots,s;\ j=1,\ldots,J;\ k=1,\ldots,K. \tag{1}$$

The dynamic behavior of this reaction in an open gradientless isothermal reactor is described:

$$x_j' = \sum(a_{-ij} - a_{ij})(r_i - r_{-i}) \equiv f_j, \tag{2}$$

$$A_k' = \sum(b_{-ik} - b_{ik})(r_i - r_{-i}) + q^0A^0{}_k - qA_k \equiv g_k\,, \tag{3}$$

where x_j – the concentration of the intermediates, $r_{\pm i}=k_{\pm i}\prod_j x_j^{a\pm ik}\prod_k A_k^{b\pm ik}$ – rates of forward and reverse elementary steps, $k_{\pm i}$ – the rate constants of the elementary step, q^0 and q are the space velocities of the main reactants at the reactor inlet and outlet, and A_k are the concentrations of the main reactants at the reactor inlet and outlet. Initial conditions:

$$x_j(t_0) = x_j^0,\ A_k(t_0) = A_k^0. \tag{4}$$

The steady states $x_{j\infty}$ and $A_{k\infty}$ will be determined from the $f_j = g_k = 0$ conditions. The results of the unsteady-state experiment will be represented as discrete sets of concentrations A_{kn} depending on time t_n varied in $h = t_n - t_{n-1}$ steps, where $n = 1, 2, 3, \ldots$ is the measurement number. We will choose, out of these sets, a number of data points necessary for the calculations and will substitute these data into Eq. (3). This will yield the following system of equations for determining $2s$ unknown rate constants of the steps:

$$A_{kn}' = \sum(b_{-ik} - b_{ik})(r_i - r_{-i}) + q^0A^0{}_{kn} - qA_{kn} \equiv g_{kn}(k_{\pm i}, x_{jn}, A_{kn}),\ k=1,\ldots, K. \tag{5}$$

The concentrations of the intermediates must be eliminated from system (5) for the inverse problem to be solvable. This can be done using unsteady-state kinetic laws of conservation (KLCs), which are derived from Eqs. (2) and (3) using their linear combinations:

$$x_j' + \sum_k \alpha_{km} A_k' = \sum_k \alpha_{km}(q^0A^0{}_k - qA_k),\ j=1,\ldots,J;\ k=1,\ldots, K;\ m=1,2,\ldots,M. \tag{6}$$

where α_{km} – integer parameters related to the stoichiometric coefficients, m is the KLC number, and M is the number of KLCs. These KLCs are independent of the rate constants of elementary steps, and can be approximately described by iterative formulas obtained by replacing the derivatives in (6) by finite differences:

$$x_{j,n}^{*} \approx x_{j,n} = x_{j,n-1} + \sum_k \alpha_{km}(q^0A^0{}_k - qA_{k,n-1} - A_{kn}')h,\ \ n=1,2,3,\ldots,N. \tag{7}$$

For the solution of (5) - (7) and determining the unknown constants of rate steps used instantaneous velocity change rate of reactant concentrations and nonlinear relaxation time. We present examples of employing this method.

PP-29

Activity of the heterogeneous uranyl modified catalysts in the gas-phase photooxidation reactions

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TiO_2 is the most investigated photocatalyst over the past decades in the field of environmental cleanup including purification of indoor and outdoor air, self-cleaning materials, bactericidal activity and water purification. It is inexpensive, chemically and photochemically stable material which could provide photocatalytic oxidation of almost any organic species. Carbon dioxide and water are the ultimate products of photooxidation. Unfortunately, TiO_2 works only in the near-ultraviolet region ($\lambda < 380$ nm), which takes about 4 % of the solar spectrum. At the same time visible light occupies about 43 % of sun irradiation. Various approaches have been examined to extend the spectral response of TiO_2 to the visible spectrum in order to utilize solar irradiation better [1].

It is well known that uranyl ions in water could be synthesized by visible light and after excitation the oxidizing potential of uranyl ions becomes as high as 2,6-2,7 V [2] but the gas phase photocatalytic oxidation (PCO) of organic species with uranyl-modified photocatalysts was weakly investigated.

In the current work photocatalyst samples were synthesized by incipient wetness impregnation method with the use of TiO_2, γ-Al_2O_3 and SiO_2 as support. The activity of catalysts was measured in the reaction of acetone and ethanol vapor photooxidation under UV and visible light irradiation.

Alumina and silica based photocatalysts demonstrated almost the same photoactivity whereas the titania based photocatalyst had at least a three times higher rate of the CO_2 accumulation in acetone PCO reaction All the samples are active under the visible light irradiation up to 500 nm wavelength [3]. Extremely high photocatalytic activity of uranyl modified titania to compare with silica and alumina under visible light was investigated with XPS *in-situ* method. It is shown that uranium is more labile on the titania surface and reduced to U^{4+} species whereas on the surface of uranyl modified silica and alumina only to U^{5+} species.

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0016 for Boreskov Institute of Catalysis.

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Multi-emitter heterogeneous chemiluminescence in system «$(NH_4)_2Ce(NO_3)_6$-C_6H_6-H_2O»

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It is well known that the reduction of Ce^{4+} to Ce^{3+} is the basis of many practical applications: initiation of radical polymerization, cerimetric method of analysis, the oxidative transformations of different classes of inorganic and organic compounds, including, water, etc. [1, 2]. Among them worth noting the chemical processes with formation the products of the reaction in electronically excited states. Chemiluminescent reactions of Ce^{4+} ions are commonly used for the analytical determination of tetracyclines, flavonoids, phenolic compounds, etc. [3]. Despite on intensive investigations in this field, the chemiluminescence (CL) occuring upon the water oxidation under action of Ce^{4+} ions was still unknown.

In this paper we describe the first example of CL occuring in the system «$(NH_4)_2Ce(NO_3)_6$-C_6H_6-H_2O». The observed CL is different from other known chemiluminescent reactions by unusual combination of various in nature emitters, namely, electronically excited states, of the Ce^{3+*} ions (λ_{max} = 335 nm), singlet oxygen $^1O_2$ (emission near 1270 nm) and its dimer $(^1O_2)_2$ (λ_{max} = 490, 645, 715 nm) [4]. The Ce^{3+*} ions and oxygen emitters $^1O_2$ and $(^1O_2)_2$ are generated in the reaction of Ce^{4+} with water and hydrogen peroxide, respectively. CL is generated only in a heterogeneous system «$(NH_4)_2Ce(NO_3)_6$-C_6H_6-H_2O» and completely absent in a homogeneous solution $(NH_4)_2Ce(NO_3)_6$ in water. This is due to the fact that the redox processes and CL in the studied system are induced by active surface of the $(NH_4)_2Ce(NO_3)_6$ crystals. It is through the action of the active surface of $(NH_4)_2Ce(NO_3)_6$ crystals is carried out population at such a high level of energy as a $5d^1$-excited state of Ce^{3+*} ion (λ_{max} = 353 nm, 3.7 eV).

The observed CL is the first example of experimental registration of excited Ce^{3+*} ions in a chemical reactions. Previously the formation of Ce^{3+*} in chemiluminescent reactions only assumed, including in many biochemical systems.

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PP-31

A new traveling wave phenomenon of endothermic reaction in catalytic fixed bed reactor under microwave heating

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The emergence of traveling wave (heat wave or else autowave) in catalytic fixed bed reactor is a subject of big interest in the theory of chemical engineering (unsteady-state processes) [1]. The traveling wave phenomena in heterogeneous media is a spatiotemporal structure, which can form in the layer because of self-organization process and were extensively studied in the 1970s and 1980s. The phenomenon of traveling wave means a self-sustained nonlinear wave process (including stationary structures) whose characteristics (propagation velocity, period, wave (impulse) length, amplitude, and shape) remain unaltered due to an energy source distributed in the medium. Thus there is ample mathematical theory for the existence of traveling wave solutions to parabolic systems of equations. One of the most interesting aspects of the theory of nonlinear waves in active distributed systems is the question of traveling waves of endothermic reactions.

This paper presents a new phenomenon in a packed bed catalytic reactor under microwave heating - traveling wave (moving reaction zones) endothermic chemical reaction. A two-phase model is developed to simulate the nonlinear dynamic behavior of the packed bed catalytic reactor with an irreversible first-order chemical reaction [2]. The absorbed microwave power was obtained from Lambert's law. Numerical analysis of mathematical model confirmed the possibility of emergence of the phenomenon of space-time dissipative structure in a packed bed catalytic reactor with endothermic reaction occurring under microwave heating. Emergence this phenomenon is the results of cooperative interaction between subsystems – filtration of a reaction mixture, effective thermal conductivity of a catalyst bed, endothermic chemical reaction, and microwave heating. Movement of the wave in the catalyst bed takes place under the influence of two factors: convective flow of the cold reaction mixture, and effective thermal conductivity. In addition, these factors act in opposite directions. The effects of the gas velocity and microwave power on performance of the packed bed catalytic reactor were presented.

One of the main roles in the mechanism of space-time dissipative structures is played by distributed energy source and this energy source can be of any nature, not necessarily chemical. Our idea of finding conditions leading to the appearance of endothermic reaction waves under the influence of microwave radiation proved to be productive.

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Modelling of the copolymerization of styrene with maleic anhydride in a homogeneous environment

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In the modern industrial production methods are increasingly used mathematical modeling of technological processes, allowing to solve problems of prediction and optimization of production. Currently, one of the most urgent problems in conducting experimental studies is the problem of extracting the maximum amount of useful information on the investigational process at minimal cost. In solving production problems and insufficient knowledge of the mechanisms of the processes is not always possible to perform a sufficient number of required experiments. In this regard, the development of a mathematical model is an actual job.

Copolymers of styrene with maleic anhydride are important commercial products and used in various industries. The kinetic scheme of polymerization of styrene with maleic anhydride comprises the following elementary steps:

1. Initiator decomposition $I \xrightarrow{k_i} 2R$,
2. Chain growth $R + M \xrightarrow{k_{i1}} P_1$,
3. The continuation chain $P_i + M \xrightarrow{k_p} P_{i+1},\ i \ge 1$,
4. Chain termination as a result of interaction with the radical $P_n + R \xrightarrow{k_r} Q_n$,
5. Chain termination by recombination $P_n + P_m \xrightarrow{k_{rec}} Q_{n+m}$,
6. Chain termination disproportionation $P_n + P_m \xrightarrow{k_{dis}} Q_n + Q_m$.

The paper presents a mathematical model based on the kinetic scheme of the copolymerization of styrene and maleic anhydride was built. The mathematical model is a system of ordinary differential equations whose dimension tends to infinity, because of the infinite number of the reaction components. Applying the method of statistical moments, infinite system of ordinary differential equations is reduced to a system with a finite number of equations and becomes solvable.

The constructed model was tested on experimental data obtained in a scientific laboratory of polymer chemistry of the Bashkir state University.The experiment was conducted on the next boot of the reagents: solvent (acetone) 400 ml, the monomers in the ratio 1:1, maleic anhydride 55 g., styrene 55 g., the initiator(porofor) 0.5 g.

Numerical solution of the target system to determine the average molecular properties such as number average and weight average molecular weights and polydispersity index.

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PP-33

Polyfunctional Surface of the Giant Polyoxometallates Mo_{138} and Mo_{132}: Photosensitized Properties

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The giant nanoclustered polyoxomolybdates (POM): $(NH_4)_{32}[Mo^{VI}_{110}Mo^{V}_{28}O_{416}H_6(H_2O)_{58}(CH_3COO)_6]\cdot(\approx 250)H_2O=Mo_{138}$ (toroidal, d=3.6 nm) and $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot(\sim 300H_2O)\cdot(\sim 10CH_3COONH_4)=Mo_{132}$ (fullerene-like, d=2.9 nm) are ones of the most perspective basis for the supramolecular inorganic-organic materials with polyfunctional (particularly catalytic) properties and template synthesis strategy. In aqueous solution POM is readily dissolved forming multicharged macroanions which could be functionalized by the electrostatic interaction, van-der-waals force and hydrogen bonds. We used above mentioned approach to create a new type of ion associates based on the nanoclustered POM (Mo_{138} or Mo_{132}), xanthene dye rhodamine-B (RhB) and the single charged cationic surfactant (dodecylpyridinium chloride). The interaction of dye molecules with POM could be appearing in the photosensitization of the catalytic activities of POM. And the controlled surfactant adsorption allows to changing the polar/nonpolar surface's properties that is important to selectivity of the catalytic process. At the first stage we produced the series of the aqueous solutions with different molar ratios POM/RhB: from the 1/1 to isoelectric point at ratios 1/32 (for Mo_{138}) and 1/46.5 (for Mo_{132}), $C[Mo_{138}]=4.2\text{x}10^{-6}$ mol/l and $C[Mo_{132}]=2.7\text{x}10^{-6}$ mol/l. By extracting the free RhB molecules from water to equal volume of chloroform and measuring their concentration by the absorbance at the characteristic wavelength (taking into account the distribution coefficient of pure RhB between phases water/$CHCl_3$), the adsorption isotherms were determined. The assessed value of the free energy ΔG(adsorption) for system «Mo_{138}-RhB» is 43.7 ±0.6 kJ/mol. The grate changes in the optical properties of RhB occurred after interaction with POM's surface during the growing of RhB concentration: the fluorescence quenching of dye in several dozens of times, the red-shift of HOMO-LUMO absorbance band of RhB (558→567 nm) and significant intensity increasing of the red-shifted band of the dye's H-dimer (522→535nm) formed on the POM's surface. Furthermore, the new band 588 nm is revealed in the UV-Vis spectrum and the transition from the RhB-monomer fluorescence (at 590 nm) to florescence of the RhB's J-aggregates (at 617 nm) is going. At the second stage we mixed the system «Mo_{138}-RhB» with surfactant dissolved in chloroform. This leaded to transfer the J-aggregates formed on the template (i.e. POM's surface) to organic phase owing to all dye's dimmers (aggregates) were forced out by the electrostatic adsorbed surfactant molecules. Thus we have made the technique to creation of the hybrid ion associates «POM(Mo_{138} or Mo_{132})-dye-surfactant» with tunable surface properties.

PP-34

Synthesis of ceolites intended for conditioning of hydrocarbon gases, containing unsaturated compounds, on the bases of the kaolins containing impurity compounds

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In work results of study of methods of synthesis and properties of ceolite sorbents of type A, including the exchange forms obtained by crystalline modification of kaolinite are introduced.

In the course of the adsorptive dewatering of hydrocarbon gases containing unsaturated compounds (ethylene, acetylene, etc.) takes place as accumulation of hydrocarbon compounds in sorbent grain at incomplete desorption, and oligomerization of the last in case of presence of surface active sites that as a result leads carburizing of layer and activity loss. In particular, the metals which are present in feed stock, in certain conditions it can develop undesirable catalytic activity.

In this connection studies on obtaining exchange forms ceolite sorbent of type A taking into account complete mineral composition of a feed stock (Angren kaolin) are conducted. At obtaining potassium forms of sorbent the way as forward exchange of ion Na^+ for ion K^+ from aqueous solution of potassium salt, and through obtaining interim ammonium forms is investigated. It is known that at an exchange of 35 % of ions of sodium for an ammonium ion, ceolite A completely conserves the pattern at the subsequent desorption of ammonia. Thus partially hydrogen form of ceolite is formed. For this reason we carried out testing of a surface of granules of adsorbent by detecting instruments Gammet at certain stages of obtaining exchange forms of ceolite. From the attained data follows that as a result of the conducted ion exchange and furnacing at 400 °C on sorbent surface there are more acid centres with $pK_a \leq 3,8$, and the basic centres with $pK_a \geq 9,3$, present at a small amount on a surface of this sample in the sodium form disappear. At increase in the soak period of this sample in a benzene solution of the detecting instrument with $pK_a + 1,5$ (benzeneazodiphenylamine) the surface of samples turns in blue colour, caused, most likely, presence of the oxidising centres. For the samples heat-treated at 170 °C, at the same time decolourization adsorbed on a surface of samples of the detecting instrument with $pK_a + 3,8$ (bromphenolblue) with transferring from acid in the basic form is noted.

Possible breaking down of crystalline structure and sample amorphicity it was valued on the variation of adsorption of water vapour. So, the sample heart-treated at 170 °C for 3 hours, at relative moisture content of 40 % adsorbs 7 g/100 g of water vapour. The sample heat-treated at 400 °C and 9 hours at 170 °C, 13 g/100 g. For samples of the potassium form of the adsorbent obtained from ammonium forms, after rehydration it is noted the increase in the adsorption of water vapour to 22,0 g/100 g.

PP-35

Synthesis and study of photocatalysts $Zn_{1-x}Cu_xO$ (0 ≤Cu ≤ 0.2)

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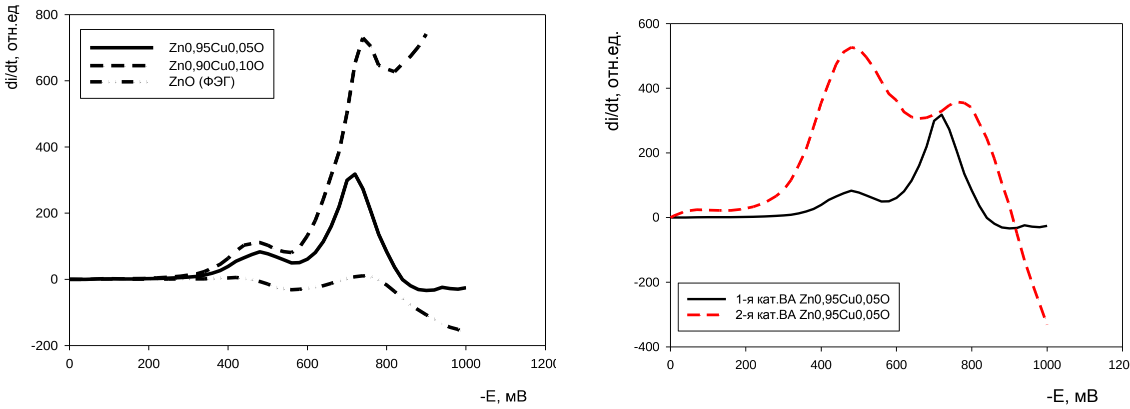
The method of precursor synthesis of $Zn_{1-x}Cu_xO$ solid solutions and $Zn_{1-x}Cu_xO/CuO$ nanodispersed composite materials with the enhanced optic range of activation of photocatalytic properties was used. As the precursor served mixed formiate $Zn_{1-x}Cu_x(HCOO)_2{\cdot}2H_2O$. This composition is a product of isomorphous replacement of Zn in $Zn(HCOO)_2\cdot 2H_2O$ by Cu. During thermolysis this composition by isomorphic transformation react to form solid solutions $Zn_{1-x}Cu_xO$ ($0 \le Cu \le 0.1$) or hybrid materials $Zn_{1-x}Cu_xO/CuO$ (x>0.1). The type of final product depend on concentration of Cu. According to the data of optical and ESR-spectroscopy Cu in these compounds occur in multivalent state. Besides, ESR-spectra of $Zn_{1-x}Cu_xO$ shows the line with g-factor near the spin value of 2.00 ($\Delta H_{pp} = 5$ Gs), belonging to singly-charged oxygen vacation V_O^+. For the determination of Cu valence distribution was used volammetry with carbon-paste electroactive electrode. On the catodic part of the curve one can see 2 peaks of Cu reduction $Cu^{2+} \rightarrow Cu^+$ (E = -480 mV) и $Cu^+ \rightarrow Cu^0$(E= -720 mV). According to the intencity of peaks may be concluded, that Cu(I) dominate in the composition of solid solutions. The repetitive polarization all Cu go to Cu(II) (Fig. 1). During the analysis of Zn(Cu)O/CuO composites we fixed the shift of the reduction wave to more negative potential and integration of reduction waves of Cu (I) and Zn (II).



a b

Fig. 1. Voltammetric curves of $Zn_{1-x}Cu_xO$ fixed:
a – at first polarization; b – at repetitive polarization

Thus, ESR data and the variation of voltammetric curves indicate about the CuO influence on ZnO electronic structure and allws us to say about the presence of contact phenomena between ZnO matrix and the coating CuO layer. It is similar to the composite compound of “core-shell” structure. The obtained materials possessed the enhanced photoactive characteristics in visible light range.

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PP-36

Scientific legacy of Georgy K. Boreskov: Bibliometric and thematic analysis

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For publications of Prof. Georgy K. Boreskov, Full Member of the Russian Academy of Sciences, referred in the Web of Science (WoS), Scopus, Chemical Abstracts Plus (CAPlus) and Russian Science Citation Index (RSCI) databases, bibliometric and thematic analysis has been performed. For the period 1929-1988, ca. 530 unique articles in periodicals and ca. 70 in non-periodicals have been collected together with 17 monographs and ca. 100 patents (Fig. 1). Obtained bibliometric statistics of Prof. Boreskov research legacy shapes his scientific school together with his strong impact in the field of fundamental and applied catalysis. Most frequently, his articles have been published in Kinetika i Katalyz / Kinetics and Catalysis (174 / 53), Doklady Akademii Nauk (90) and Reaction Kinetics and Catalysis Letters (42) journals. His most active coauthors have been V.V. Popovsky and V.D. Sokolovsky with 55 and 50 joint articles, respectively. The most cited original article (WoS, 220) and monograph (WoS, 232) have been G.K. Boreskov, The catalysis of isotopic exchange in molecular oxygen, Adv. Catalysis, **1964**, 15, 285-339, and G.K. Boreskov, Geterogennyi Kataliz, Nauka Publishers, **1986**. 303 pp.

Figure 1. Dynamics of Prof. Boreskov publications

Thematic analysis based on controlled terms of the CAPlus database allows tracing the main directions of his research and highlighting its broad scope. Most frequently his journal and patent publications have been assigned to the *Catalysis and Reaction Kinetics / Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms* (281 / 95) Section, and to the *Oxidation catalysts* (241) CA Concept Heading.

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PP-37

Ru-Ba-Cs/Sibunit catalysts for ammonia synthesis: the investigation of carbon support stability

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Carbon supported ruthenium catalysts are widely used in Haber-Bosch, Fischer-Tropsch processes and other reactions. It is known that carbon support can degrade in reducing atmosphere due to hydrogenation to methane by hydrogen dissociated on platinum metal particles. It was found for Ru/Sibunit catalyst that the process of support methanation in ammonia synthesis may be suppressed by alkali metal promotion.

The purpose of this study was to investigate the influence of promoter concentrations on the stability of carbon support in Ru-Ba (Cs)/Sibunit catalysts.

The experiments were carried out in a quartz fixed-bed reactor in 3 stages: 1) the heating until to 500 °C in He with the rate of 10 °C/min; 2) keeping the sample under He atmosphere at 500 °C during 10 min; 3) replacement of atmosphere from He to H_2 with subsequent heating of the sample for 5 hours. The outlet mixture was analyzed using a gas chromatograph equipped with a flame-ionizing detector.

We have found that the doping of Ru/Sibunit catalyst by barium allows to decrease amount of carbon loss as a result of support methanation up to 4 times as compared with cesium doped catalyst (Fig. 1). The influence of barium consists in the suppression of methanation activity of ruthenium particles due to interaction with barium (barium oxide) particles which are located near ruthenium. As seen in Fig. 2, the type of the methanation curve strongly depends on the nature of alkali metal in Ru-Ba (Cs)/Sibunit catalyst.

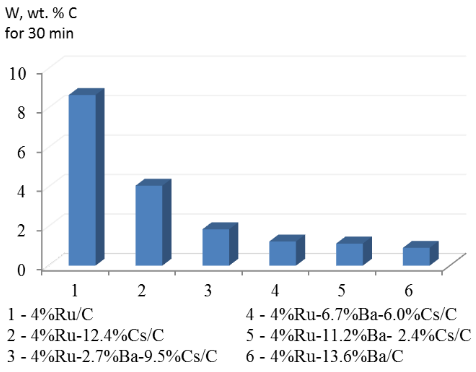

Fig. 1. Carbon transformation to CH_4 (30 min, 500 °C, H_2)

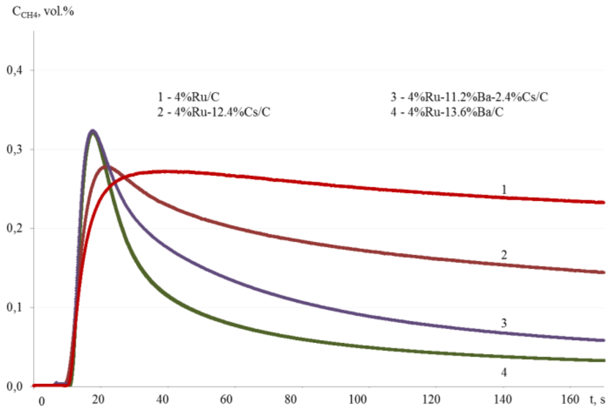

Fig. 2. Carbon support methanation curves (500 °C, H_2).

PP-38

Catalytic Technologies for Purification of Gas Streams from Hydrogen Sulfude

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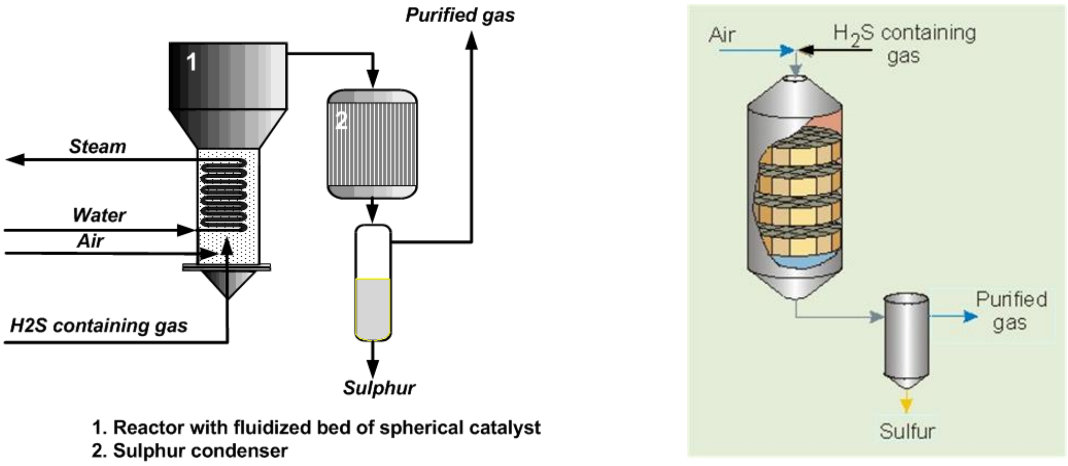
Introduction

More than 40 % or > 70*10^{12} nm^3 of the world's hydrocarbon gas reserves are hydrogen sulphide containing natural and oil-associated gases [1]. This feedstock is a significant potential resource for energetics and chemical synthesis. However, high content of hydrogen sulphide (1-30 vol.%) excludes direct application of these gases as fuels or raw materials for downstream production. The currently used flame combustion of such gases leads to air pollution with toxic sulfur di- and trioxides, sulfuric acid, products of incomplete combustion of hydrocarbons, and carcinogenic soot, amount of which attains one million tons a year. Thus, the development of the technical solutions for reliable on-site purification of these gases is a problem of the highest priority for the Russian Federation and the whole world.

Experimental/methodology

Technology of direct selective oxidation of hydrogen sulphide.

In the Laboratory of Environmental Catalysis of the Boreskov Institute of Catalysis, new processes based on direct catalytic oxidation of hydrogen sulphide were developed [2-3]. The technology is schematically depicted in Fig. 1.



Version 1
Hydrogen sulphide oxidation in reactor with fluidized bed of catalyst
Rich gas purification (CH_2S = 10- 95 %)

Version 2
Hydrogen sulphide oxidation in reactor with fixed bed of catalyst
Lean gas purification (CH_2S = 0,1- 10 %)

Figure 1: The technologies of direct selective oxidation of hydrogen sulphide

The technologies was successfully tested in pilot and industrial scale on the largest sour gas fields, refineries and gas processing plants in Russia [3-6].

Industrial installations of direct selective oxidation of hydrogen sulphide.

The general view of the industrial installations is presented in Fig. 2.

Reactor with fluidized bed of catalyst

Reactor with fixed bed of catalyst

Figure 2: Industrial installation for direct selective oxidation of hydrogen sulphide

Results and discussion

The efficiency of hydrogen sulphide removal was proved to exceed 99%.

During two years of continuous operation:

- 400 10^6 m^3 of commercial gas were produced;
- 2500 tons of hydrogen sulphide were recovered as elemental sulfur;
- emission of more than 5000 tons of sulfur dioxide and sulfuric acid to the atmosphere was prevented;
- pollution damage for the amount of $ 10 million was averted.

Characteristics of the produced sulfur surpass those specified by Russian National Standard #127.1-93 (commercial grade sulfur 9990).

Conclusions

The technologies for purification hydrocarbon feedstock based on direct selective oxidation of hydrogen sulphide has been developed. The efficiency of the technology has been proved upon field testing of an industrial installations.

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The effect $Ni_xCo_{3-x}O_4$ (x = 0-1) composition and modification of Cs cations on catalytic activity in de-N_2O reaction

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Nitrous oxide is a contributor to the destruction of ozone in the stratosphere and a strong greenhouse gas. A reduction of N_2O emission from industrial sources is indispensable. Cobalt based spinels $M_xCo_{3-x}O_4$ (M = Mg, Ni, Zn, Cu) were found to be highly active catalysts for N_2O decomposition from tail gases in HNO_3 production [1]. The mechanism of the reaction proposes N_2O dissociative adsorption on the active centre (oxygen vacancies or metal centers) whereby N_2 is desorbed while an adsorbed oxygen species stays at the surface of the catalyst. Desorption of adsorbed O species was found to be the rate-determining step of the N_2O decomposition reaction. The addition of alkali metal dopants increases the catalyst activity in the reaction. The aim of this work is to determine the effect of Co-Ni-spinel composition and the Cs cations modification method on the properties of $Ni_xCo_{3-x}O_4$ catalysts and their activity in nitrous oxide decomposition at low temperatures.

$Ni_xCo_{3-x}O_4$ (x = 0-1) catalysts were prepared by co-precipitation from nitrate solutions using $(NH_4)_2CO_3$ as the precipitant that clearly eliminates the ingress of the alkali metal cations in the initial composition of the catalyst. Cs (1-3 %) modifying cations performed (a) by impregnating the dry precipitate (powder precipitated carbonates and bicarbonates Ni^{2+} and Co^{2+}) $CsNO_3$ solution or (b) by the polymerizable complex method using citric acid and ethylene glycol. Then the samples were calcined at a temperature of 450-500 °C for 2 hours. The activity of the catalysts tested in the decomposition reaction of N_2O at 130-430 °C under various model mixtures containing N_2O, O_2, H_2O in helium and a contact time of 0.5 sec. Prepared catalysts were studied with XRD, XPS, BET, TPR and TPD-O_2 methods to clarify the influence of the catalyst composition on the catalyst activity and oxygen vacancies content to elucidate the nature of active sites.

It was found that the catalytic activity of $Ni_xCo_{3-x}O_4$ spinels in N_2O decomposition reaction depends on the several factors: the degree of substitution (x), the amount of Cs cations, and the modification method. TPR and TPD measurements indicate that the presence of Cs reduces M-O binding energy and results in formation of weakly bound oxygen forms. This can cause an increase of catalytic activity in N_2O decomposition in comparison with unmodified samples as far as the desorption of oxygen from the catalyst surface being the limited step of the process.

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PP-40

Application of Ag L_α Radiation for XPS Study of Pt- and Au- Based Catalysts

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X-ray photoelectron spectroscopy has proved itself as a powerful tool for the study of processes on the surface of heterogeneous catalysts. Nevertheless, the use of non-standard radiation Ag L_α (hv = 2984.3 eV), which leads to the excitation of additional (compared with standard radiations Mg K_α or Al K_α) deep-lying levels, can significantly enhance the potential of the XPS method [1]. For instance, in the study of Pt-containing catalysts on alumina-based supports, the Ag L_α radiation helps to avoid the overlapping of XPS lines due to Pt 4f and Al 2p. In this case, the study of a Pt state on the basis of the analysis of the Pt $3d_{5/2}$ line provides the possibility to determine the nature of the active site for a number of hydrocarbon conversion catalysts [2-5]. The use of the Davis technique for model planar samples Au/HOPG by comparing the intensities of the lines Au 4f and Au $3d_{3/2}$ provides data on the size of surface Au particles [6]. In addition, comparison of results of XPS and STM methods makes it possible to determine the shape of the Au particles. It was found that on a smooth surface of fresh HOPG, Au particles have a spherical form. In contrast, on the surface of the defect surface, prepared by treating the fresh HOPG with argon ions, the interaction Au-C increases and the particles take the form of a hemisphere and a truncated hemisphere. The possibilities of application of this technique for porous Au/C samples, as well as for Pt-based catalysts, are discussed.

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PP-41

Development of a local structure of the M1 phase in VMoNbTeO catalysis for C_2-C_3 oxidative transformations

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To date, the most effective catalysts for low-temperature ethane and propane transformations are $Mo_1V_{0.2-0.4}Te_{0.20-0.25}Nb_{0.10-0.18}$ oxide compositions. According to the literature, the catalytic activity and selectivity of such catalysts is attributed to the so-called M1 phase. To obtain the M1 phase, all the components should interact already at the step where a wet precursor is synthesized, which is reached in a narrow range of pH values. Chemical composition, drying and the sequence and conditions of heat treatment also exert a substantial effect on the phase composition of the samples.

The goal of the present work is to study the development of the local structure of the M1 phase starting from the solution of components using EXAFS and Pair Distribution function (PDF) methods. We used EXAFS spectroscopy for Mo-K and Nb-K edges to study the structural evolution starting from the mixed VMoTe solution to VMoTeNb gel, amorphous spray-dried sample and highly disordered oxide precursor formed after calcination.

X-ray data were collected at beam line 11-ID-B, APS, Argonne at an energy of 58.26 keV, i.e. $\lambda = 0.2128$ Å. Mo- and Nb-K X-ray absorption spectra were recorded on an EXAFS station at the Siberian Synchrotron Radiation Center (Novosibirsk) using the standard transmission procedure. The spectra were recorded at electron energy of 2 GeV in the VEPP-3 ring and a current of 80 mA.

It was demonstrated that an Anderson-type heteropoly compound is formed in the VMoTe solution. Nb addition and spray drying does not change the local structure around Mo atoms. Nb in the VMoTeNb gel forms Nb-O-Nb bonds, which length corresponds well to the Nb_2O_5. The spray-died sample become amorphous after calcination in air at 300 °C. The further calcination at 400-500 °C results in the formation of nanocrystalline domains. The local structure of the nanocrystalline domain was simulated using the PDF data. It was shown that the atomic arrangement of the nanocrystalline domain is similar to the M1 structure.

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Investigation of catalytic hydrothermolysis of ammonia borane

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The diminishing natural energy resources and the increasing pollution of the environment require new types of fuels. In this respect, hydrogen is the most appealing choice provided that there will be a compact, self-contained and safe H_2 storage systems meeting the international requirements for hydrogen storage. The problem could be solved through the use of inorganic hydrides among which ammonia borane (NH_3BH_3, AB) is the leader in terms of the mass (19.6 wt.%) content of hydrogen and stability in air.

H_2 can be produced from NH_3BH_3 in various ways – via methanolysis, thermolysis, hydrolysis, hydrothermolysis, among which AB hydrothermolysis has a number of advantages because of its high energy efficiency. The process involves an exothermic hydrolysis and thermolysis of AB, the latter process requiring a prolong heating to start H_2 generation. In addition to this, the polar molecules of water have a destabilizing action on the dihydrogen bonds in the ammonia borane crystal structure thus enhancing the mobility of the hydrogen. To date, the literature has dealt only with the non-catalytic hydrothermolysis of ammonia borane. The reaction proceeds at 90 °C and ensures a gravimetric energy capacity of 7.7 wt.% H_2 [1].

This work presents results on the catalytic hydrothermolysis of NH_3BH_3 using complex oxides and chlorides of transition metals. It was found that these compounds allow an increase in the yield and rate of hydrogen generation as well as a reduction in the process temperature to as low as 80 °C. It was demonstrated that the catalytic effect of transition metal compounds was a result of their reduction by the hydride medium to form a highly dispersed catalytically active phase.

Photocatalytic hydrothermolysis of NH_3BH_3 has been investigated for the first time – a process where hydrogen evolved more intensely when the hydrogen-generating composite was illuminated by light with wave lengths of 365, 450 nm and TiO_2 was used as a photocatalyst. It was established that modification of the TiO_2 with colloid silver increases the yield and the rate of hydrogen generation. The efficiency of this process depends on the nature of the support, the content of Ag, and also on the illumination wave length.

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Structural self-organization of solid state products during interaction of halogenated compounds with bulk Ni and Ni-Cr alloy

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Recently [1-3] we have revealed an opportunity to use the bulk metallic nickel and some of its alloys (Ni-Cr, Ni-Cu) as precursor for catalysts active in synthesis of carbon nanomaterials (CNM) via decomposition of halogenated hydrocarbons. It was found that during catalytic reaction massive metallic hardware (piece of Ni-foil or Ni-Cr wire) undergoes profound structural changes known as ‘metal dusting’ or ‘carbon erosion’. Under aggressive action of reaction atmosphere containing chlorinated hydrocarbons the initial bulk Ni-alloy can be completely wasted into uniform nickel particles of about 200-250 nm in size to play further the role of active sites for catalytic growth of carbon fibers. During the catalytic process of CNM growth the gas-phase reaction products (HCl, CH_4 etc.) are removed from the reactor by the reaction flow. For the purpose to identify the possible solid-phase intermediates we have studied the similar process in the closed reaction volume (actually, in autoclave conditions) when there is no removal of gas-phase products from reaction volume. In literature such approach was named as RAPET (Reactions under Autogenic Pressure at Elevated Temperature) [4-5].

Transformations of the Ni-Cr alloy (nichrome) under the RAPET conditions during interaction with various halogenated hydrocarbons have been studied. Formation of the metastable solid-phase intermediates (nickel halides) is revealed. These species are believed to play an important role in catalytic corrosion of nickel and its alloys and, perhaps, in the processes of catalytic growth of carbon nanomaterials via decomposition of halogenated hydrocarbons. High sensitive FMR technique which allows one to detect emergence of nickel nanoparticles in the course of catalytic corrosion of bulk Ni-Cr alloy has been proposed. This method was shown to be rather effective for *in situ* diagnostics of the Ni-containing samples exposed to RAPET conditions.

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Effect of the alumina phase transformation on stability of low-loaded Pd-Rh three-way catalysts

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Among platinum group metals palladium and rhodium attract much attention as active components of different oxidation catalytic systems including three-way catalysts (TWC). In the latter, the joint using of Pd and Rh provides an efficient oxidation of CO and hydrocarbons along with NO_x reduction. Thermal deactivation of three-way catalysts is known to becaused by several processes which take place in temperature range of 800-900 °C and even lower depending on starting materials. It leads to noticeable decrease of surface area as a result of sintering and high-temperature solid-state transformations. In turn, sintering of precious metals becomes significant at 600 °C. Mechanism of sintering of dispersed metal particles assumes it surface diffusion or, in the case of high temperatures, mobility of large agglomerates. The temperature at which solid phase becomes mobile depends on such factors as texture, size and morphology. Thus, porous γ-Al_2O_3 is much more sensitive to sintering than nonporous α-Al_2O_3. The temperature of the procedure can differ depending on the conditions of aging and the studied factors, however, it usually lies within the range $800 \leq T_{ag} \leq 1300$ °C. The behavior of catalytic systems at a temperature up to 1000-1050 °C is being particularly interesting. We should note that at the high temperatures the phase changes of γ-oxide to δ (above 800 °C) and further to θ (above 1000 °C) are expected. An impact of the alumina nature (phase modification) over the deactivation of TWC catalysts is barely ever discussed in literature. The given work is dedicated to the study of this influence as well as of the role of the support phase changes in these processes. For that purpose a series of Pd-Rh/alumina catalysts with total precious metals loading of 0.2 wt.% was prepared. Recently we have shown that palladium atoms or clusters can be efficiently anchored on the surface of γ-Al_2O_3 when the loading of Pd does not exceed concentration of electron-donor sites [1]. It was shown that concentration of donor sites of the supports differs according to distinctions between values of their specific surface areas. Finally, it has been found experimentally that phase transformation of γ-Al_2O_3 at high temperatures does not play dramatic role for the deactivation of bimetallic Pd-Rh active species.

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PP-45

Separate kinetic studies of reaction steps for the catalytic oxidation of ethylene over silver films: intrinsic mechanism of the reaction

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Silver is the only known catalyst for partial oxidation of ethylene to ethylene oxide. This reaction is used to produce millions of tons of ethylene oxide, which is among the most versatile products of petrochemistry. However, high performance of silver catalysts, achieved in industry [1, 2], does not adequately reflect the intrinsic catalytic properties of silver. They are provided by the introduction of promoters into silver; among them are chlorine (in the form of chlororganic compounds), alkaline and alkaline earth metals, in particular cesium. Pure silver, which is free of foreign atoms, shows high activity, but only a minor selectivity. The intrinsic mechanism of the reaction is not quite clear.

Intrinsic features of the reaction mechanism could be revealed when kinetics of each reaction step is studied separately; the study is performed using a model silver catalyst, i.e. the pure metal having only an adsorbed layer of oxygen atoms with a variable concentration. In this work, intrinsic features of the catalytic reaction mechanism are examined in separate kinetic studies of the ethylene oxidation steps over a model silver catalyst, which is a silver film prepared by evaporation and condensation of metal in vacuum.

To reveal the mechanism of catalytic oxidation of ethylene over silver, we studied separately the kinetics of main reaction steps: the adsorption of oxygen and interaction of adsorbed oxygen with gaseous ethylene. The study was performed in the temperature range of 373-473 K at the oxygen and ethylene (C_2D_4) pressure of about 1 Pa and the initial surface coverage by adsorbed oxygen $\theta = 0.42$. It was shown that oxygen adsorption causes essential changes in the surface properties of the silver catalyst. The revealed dependences for the rate of partial and complete oxidation steps on the surface coverage by oxygen have the wave shape with a maximum. This gave grounds to suggest the intrinsic features of reaction mechanism: the primary steps of partial and complete oxidation of ethylene take place on the oxygen-free silver surface sites surrounded by univalent silver oxide particles, which change the properties of the catalyst surface. [3, 4].

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PP-46

The active species of Rh/CeOx catalysts: XPS and TPR CO study

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The Rh/ceria system has been studied over the last years in order to establish the nature of the active sites and influence of interaction between CeO_2 and Rh on the catalytic performance of the system. In our work the temperature programmed reaction with CO (TPR CO) and X-ray photoelectron spectroscopy (XPS) experiments were performed to elucidate the main species of Rh/CeOx catalysts active in CO oxidation reaction.

The TPR CO curves had a complicated structure pointing to at least three types of centers active in different temperature ranges (Figure 1). The calculated ratio of consumed CO molecules per Rh atoms was ~ 4.3 implying the participation of CeO_2 lattice oxygen in the reduction process. The treatment of the samples with CO (O_2) performed directly in the photoelectron spectrometer without contact with air allowed us to establish the charging states of the components during Red-Ox processes. In the initial samples rhodium was found in the oxidized Rh^{3+} state in a composition of $Rh_xCe_{1-x}O_{2-\delta}$ solid solution ($E_b(Rh3d_{5/2})$=309.2 eV). The ($Ce^{3+}/Ce^{3+}+Ce^{4+}$) ratio was about 10-15 %. Interaction with CO up to 150 °C caused the reduction of CeO_2 surfaces ($Ce^{3+}/Ce^{3+}+Ce^{4+}$) ~25 % without significant changes of Rh state. At higher temperatures rhodium gradually reduced with formation of $Rh_n^{\delta+}$ species ($E_b(Rh3d_{5/2})$=307.8 eV) with $Rh_n^{\delta+}$/Rh ratio reaching ~80 % at temperatures higher 300 °C. The O_2 treatment of reduced surface resulted in complete reoxidation of CeO_2 to the initial state and substantial reoxidation of Rh ($Rh_n^{\delta+}$/Rh ratio ~50 %) already at room temperature.

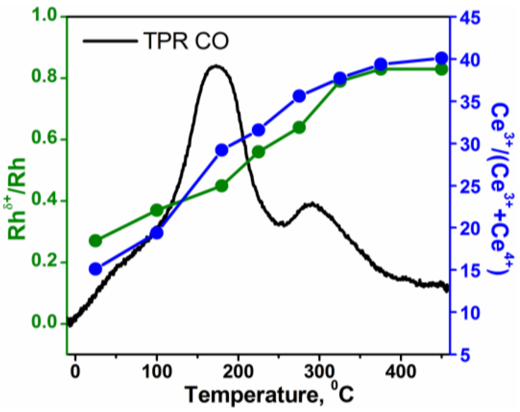

Figure 1. Combination of TPR CO and quantitative XPS results for Rh/CeOx catalyst

Incorporation of Rh^{3+} species into the lattice of cerium oxide leads to significant modification of the system properties resulting in high reactivity of the system towards reduction by CO and reoxidation by molecular oxygen even at lower temperature.

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Oxidation and etching of polycrystalline platinum in O_2 and NH_3-air flow

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Ammonia oxidation with air on platinum catalyst gauzes is widely used in chemical industry for synthesis of nitric acid. It is well known that during this process the gauzes undergo deep structural rearrangement of surface layers (catalytic etching) leading to the loss of platinum and decrease of catalytic activity. To reveal the mechanism of the catalytic etching of platinum catalyst gauzes during the NH_3 oxidation, we carried out detailed investigation of the surface microstructure of platinum catalysts treated in oxygen, and in the reaction medium (NH_3+O_2). Polycrystalline Pt foil with the size of 10 x 5 x 0.04 mm was used as the catalyst. The sample was assembled into a package with four platinum gauzes required to maintain standard conditions of the NH_3 oxidation process. A quartz laboratory flow reactor was used at the feed (ca. 10 % NH_3 in air) flow rate 880-890 l/h, the gauze temperature 1133 K and total pressure about 3.6 bar. The surface microstructure was studied using a scanning electron microscope JSM-6460 LV (Jeol).

Different microstructure of polycrystalline Pt foil was observed by SEM after the treatment of the platinum sample at T ~ 1400 K for 3 h in oxygen (21.5 % O_2 in He), and at T ~ 1133 K for 5 h in reaction medium (~10% NH_3 in air). A micrograin structure with 10-200 μm grains was formed on the surface of the sample during the reaction of O_2 with the platinum foil. The grain structure is formed during decomposition of the surface film including the graphite-like layer covering the surface of the grains and grain boundaries in the bulk of the polycrystalline sample. During the interaction of the sample with oxygen the surface graphite-like layer is destroyed due to the reaction of carbon with oxygen. During the NH_3 oxidation over Pt foil the O_2 interaction with platinum results in removal of the surface graphite-like layer followed by dissociative chemisorption of oxygen on the Pt surface. It is well known that oxygen dissolution in the Pt lattice with the formation of oxide phases is substantially slower than on other platinum metals (Pd, Rh). The O_2 interaction with Pt can lead to intense dissolving of oxygen atoms at defects. So, large amount of oxygen atoms can be absorbed at the grain boundaries and other defects. The reaction of gaseous NH_3 molecules with absorbed oxygen atoms O_{abs} with the formation of gaseous NO results in local overheating of the surface initiating the release of metal atoms to the surface. Intense release of metal atoms from the grain boundaries leads to the formation of extended voids between the grains. Adsorbed Pt atoms quickly migrate over the metal surface and get incorporated into energetically the most favorable sites. Due to these processes, pits and crystalline facets grow on the surface, whereas grains are gradually reconstructed into faceted crystalline agglomerates. So, structural reconstruction of the foil surface layer (catalytic etching) with the formation of a rough layer takes place during the catalytic NH_3 oxidation with air on Pt at T~1133 K for 5 h.

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PP-48

Photocatalytic Oxidation of Ethanol on Titanium Dioxide modified by Noble Metals under Visible Light

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Photocatalytic oxidation is being used ever more frequently for the removal of organic pollutants from the air. Modern photocatalytic purification methods are based on the use of titanium dioxide (anatase modification) as the photocatalyst. Extremely reactive particles such as electron vacancies (h+) and $OH^{\cdot}$ radicals are formed on the surface of this photocatalyst by the action of UV irradiation. The main disadvantage of TiO_2 is its ability to absorb only UV light with wavelength less than 380-400 nm. Thus, in practice, sources of artificial UV light such as mercury and xenon lamps as well as, more recently, UV LEDs are used to initiate photoreactions. On the other hand, more than 43 % of the sunlight energy is in the visible spectral range in contrast to less than 4 % for ultraviolet light. This circumstance is the major reason for the search for new photocatalysts which are active under visible light.

In the present work, we carried out a systematic investigation of the effect of additives of various noble metals (Pt, Pd, Au, Ru, and Ag) on the photocatalytic activity of Me/TiO_2 catalysts (Me = metal) by the action of visible light and its relationship to the nature of the metal. The Me^{n+}/TiO_2 samples were obtained by impregnation of TiO_2 powder using aqueous solutions of H_2PtCl_6, $PdCl_2$ or $RuCl_3$ acidified with a given concentration of HCl. The catalyst obtained was dried at 120 °C for 2 h and roasted in the air at 650 °C during 3 h.

The Me/TiO_2 samples were prepared by adding an aqueous solution of $AgNO_3$ or $HAuCl_4$ acidified with HCl dropwise to an aqueous suspension of TiO_2 with subsequent ultrasonic treatment (20 kHz) for 30 min. The metal ions were then reduced either using a three-fold excess of $NaBH_4$ or photochemically in the presence of ethanol.

Photocatalytic activity was measured in the oxidation of ethanol vapor. Under visible light the reaction proceeds substantially with formation of acetaldehyde and its formation rate was used as a measure of photocatalytic activity of the samples.

All these samples have activity upon the action of visible light ($\lambda > 420$ nm) in the oxidation of ethanol vapor with formation of acetaldehyde as the final product. The highest rate of acetaldehyde release for the Pt/TiO_2, Pd/TiO_2, and Au/TiO_2 photocatalysts was found for samples with 1 mass % metal. The possibility of the complete oxidation of ethanol to inorganic products (water and CO_2) was demonstrated for photocatalysts containing gold and platinum.

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PP-49

Photocatalytic oxidation of CO on the Pd/TiO_2 catalysts synthesized by the decomposition of $Pd(acac)_2$

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Carbon monoxide is a major concern for environmental protection. CO can be considered as either a primary pollutant from different emissions or a secondary pollutant resulting from the partial (photo)oxidation of VOCs. CO is poorly photooxidized on the pure TiO_2 photocatalyst. One of the reasons for that is a weak adsorption of CO and oxygen on TiO_2 surface at ambient conditions. The deposition of metallic nanoparticles on TiO_2 surface can enhance adsorption capacity of the catalysts and provide reactive sites for CO oxidation [2].

The aim of this study was to prepare Pd/TiO_2 photocatalysts by the decomposition of $Pd(acac)_2$ and investigate in CO oxidation at ambient conditions both without and with UV irradiation. The effect of several parameters including UV or thermal treatment, the calcination temperature, the metal content on the (photo)catalytic activity was studied.

The 0.05-4 wt.% Pd/TiO_2 catalysts were synthesized by the impregnation of TiO_2 with a certain amount of $Pd(acac)_2$ dissolved in acetone with subsequent the photo- or thermodecomposition of adsorbed $Pd(acac)_2$. In the former case, the sample was UV irradiated for 12 hours. In the latter, the sample was calcined at 210, 250 or 310 °C for 3 hours. Catalytic activity of the synthesized samples was investigated in the reaction of CO oxidation in a static reactor at ambient conditions.

The photocatalytic rate of CO oxidation under UV irradiation was up to 3.5 times higher than the rate of catalytic CO oxidation without UV irradiation. The activity of the samples prepared by the photodecomposition way was much higher than the activity of the calcined samples both without and with UV irradiation. XPS analysis revealed that the photodecomposition way results in a higher amount of metallic palladium nanoparticles on the TiO_2 surface which in turn resulted in a higher activity. An increase in the calcination temperature from 210 to 310 °C results in a decrease of the photocatalytic activity.

One of the most important results is that the photocatalytic rate of CO oxidation increased as the Pd content increased from 0.05 to 4 wt.%. TEM analysis showed that at a high metal content (e.g., 4 wt.%) the amount of particles was increased but their size and distribution was the same as in the case of the low Pd content.

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PP-50

Comparison of supported Au and Ag nanocatalysts for 1-octanol oxidation

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Nano gold-based processes are considered green alternatives to conventional processes of selective oxidation of alcohols, due to the high efficiency of Au nanoparticles (NPs) Their performance can be modulated by the selecting the support [1,2]. Ag and Au have analogous catalytic properties due their similar electronic structure, atomic size, structure, and bulk-lattice, but few works have reported catalytic oxidation of n-octanol on Ag based catalysts. Though the catalytic properties of Ag are inferior, replacing Au with Ag for this reaction type could be interesting due to its much higher availability and much lower cost, provided its performance can be boosted. We study here the catalytic activity of Au and Ag NPs supported on La_2O_3, CeO_2 and Al_2O_3 for this reaction to investigate the effect of supports' nature and the effect of the reductive and oxidative pretreatments on Au and Ag catalysts.

Catalyts (with 4 wt.% Au or 2.3 wt.% Ag) were prepared from aqueous solutions of $HAuCl_4 \times 3H_2O$ by deposition-precipitation (DP) with urea or of $AgNO_3$ by DP with NaOH, followed by vacuum drying at 80 °C for 2 h. Samples were characterized by BET, XRD and FTIR of CO adsorption and tested for octanol oxidation at 80 °C and atmospheric pressure for 4 h, using 0.1 M n-octanol in heptane with no base added, molar ratio alconol/metal = 100, and 30 mL/min O_2, either as prepared or after pretreatment in H_2 or O_2 flow at 300 °C.

In the conditions tested both Al_2O_3 supported catalysts were inactive, regardless the pretreatment. The activity of the other catalysts depended on the nature of the metal and the support and the treatment applied. As-prepared samples showed low activity, which was affected by the redox treatments in different ways depending on the metal and the support. Activity of CeO_2-supported catalysts increased with the O_2 treatment but decreased with that of H_2, while that of Au/La_2O_3 was increased by both eightfold by H_2 and by a factor of 12 by O_2 treatment, and the order of activity after oxidative pretreatment was: Au/La_2O_3 > Ag/CeO_2 > Au/CeO_2 > Ag/La_2O_3.

As these different effects of pretreatment depended on the metal and the support nature, this involves that they are not simply due to the thermal effect, and may be discussed in terms of the electronic state of the metal active centers and its evolution with the pretreatments. This opens a way to improve the performance of Ag catalysts by suitable choice of support and preteatment

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PP-51

EPR study of $MgCl_2$-supported Ti(II)-based catalysts for ethylene polymerization

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The EPR method was used to study the state of titanium ions in supported titanium-magnesium catalysts based on Ti(II) compound – $[\eta^6\text{-}C_6H_6{\cdot}TiCl_2{\cdot}2AlCl_3]$. It is known these catalysts are able to perform ethylene polymerization in the absence of organoaluminum activator [1].

In the earlier works [2, 3], EPR signals from Ti^{2+} ions were observed and studied in the spectra of compounds containing Ti^{2+} ions. For the studied Ti(II)-based supported catalysts, EPR signals were also observed at low temperature (77 K). We suppose the presence of EPR signals from titanium ions may be caused by the strong interaction of surface Ti(II) species with coordinately unsaturated Mg atoms possessing Lewis acidity, which changes the electronic state of Ti(II) atoms. The interaction of surface Ti(II) species in the catalysts with water and chloropentafluorobenzene leads to their oxidation to Ti(III) species, which are EPR observable at 298 and 77 K.

The interaction of supported Ti(II)-based catalysts with α-olefins changes their EPR spectra: a signal from Ti^{3+} ions is observed at 298 and 77 K. The data obtained suggest that interaction of the catalysts with α-olefins is accompanied by oxidation of Ti(II) to Ti(III) surface species. The formation schemes of Ti(III) species as active sites of the studied catalytic systems were proposed.

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PP-52

Design of novel solid acid catalysts for the gas-phase aromatic nitration

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Nitration of aromatics is a large-scale industrial process with global production about 4-5 million tons of commercially valuable chemicals (nitrobenzene, nitrotoluene, 2,4-dinitrotoluene) per year. In industry the aromatics nitration is carried out in the liquid phase with a mixture containing nitric and sulphuric acids. A major problem of this technology is associated with diluting of the nitration mixture by water formed as one of the reaction products. The utilization of the resulting diluted sulphuric acid (0.9 ton wastes per 1 ton of commercial product) creates considerable technological and ecological challenges [1]. The heterogeneous catalytic nitration processes could be regarded as an alternative to industrially realized nitration technique. The appearance of the innovative solid acid systems with acidity comparable to concentrated H_2SO_4 renewed interest of investigators to the heterogeneous catalytic nitration.

In present study we have prepared two types of heterogeneous catalytic systems (solid acids) for the aromatic nitration. All catalytic systems were characterized by set of methods (HRTEM, XRD, XPS; FTIR, NH_3-TPD, BET and irreversible base titration) and tested in heterogeneous aromatic nitration (benzene and toluene nitration reactions). The yield of nitroproduct was determined by GC (Crystall-2000M); concentration of NPs by HPLC (Agilent-1200). Firstly we have developed synthetic methods for sulphated perfluoropolymers (Nafion, F-4SF) deposition on carbon nanofibers (300-400 m^2/g) (or silica (SBA-15)) and studied the catalytic properties of the obtained materials. The best catalyst exhibits 99.9 % selectivity to nitroproduct with concentration of by-products (mainly nitrophenols) less than 300 ppm [2]. In the second part of our experiments we have prepared heterogeneous catalysts $M(OTf)_n$ on different supports (M= Bi, Yb; OTf – triflate anion). That type of systems acts as nitric acid acceptor which creates catalytically active high-acidity intermediate $H^+[M(OTf)_nNO_3]^-$. This is the first attempt to use these systems in heterogeneous nitration of aromatic compounds. In conclusion, Nafion/CNF, Nafion/SiO_2, $M(OTf)_n/SiO_2$ and $M(OPf)_n/SiO_2$ samples were found to have sufficiently high catalytic activity (nitrobenzene yield >85 %) and characterized by low-nitrophenols content (less than 300 ppm).

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PP-53

Humidity induced deactivation of alumina and silica supported Pd, Pt, Pd-Pt catalysts in H_2 and O_2 recombination reaction for Passive Autocatalytic Recombiners PAR

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Passive autocatalytic recombiners (PAR) are the safety devices applied in the nuclear power plant to lower the explosion risk associated with hydrogen release. In PAR hydrogen and oxygen are recombined $2H_2 + O_2 \rightarrow 2H_2O$ on Pt or Pd catalyst with strong exothermic effect. However, conventional recombiners show a considerable time delay, mostly induced by the water film covering the catalyst. Here, we focus on metal and support selection for the recombination reaction in view of catalyst interaction with water molecules.

Alumina and silica supported monometallic Pd, Pt (0.5 and 2 wt %) and bimetallic Pd-Pt catalysts (Pd/Pt : 1:2; 1:1; 2:1) were prepared by reverse "water-in-oil" microemulsion method. The catalysts were characterized by XRD, XPS, SEM-EDS, TEM, HRTEM, DTG techniques. The $H_2 + O_2$ reaction was studied in the flow reactor in reaction mixture 0.5 vol % H_2 in dry or water vapour saturated air. The H_2 conversion and the temperature of catalyst was measured. In calorimetric experiments the H_2 conversion and thermal effects were monitored vs reaction time. The energy aspects of water molecules interaction with mono- (Pd, Pt) and bi- (Pd-Pt) metallic clusters are calculated within the DFT method.

The type of support (silica, alumina) and the type of metal (Pt, Pd, Pd-Pt) are variables affecting catalytic performance in H_2 and O_2 recombination reaction in term of both activity and deactivation by water/humidity. Both water vapour present in the atmosphere as well as water formed in the recombination reaction inhibited active sites in the studied catalysts. Platinum (due to its higher hydrophilicity - larger water-metal binding energy) was more prone to deactivation than palladium. The bimetallic Pd-Pt supported catalysts were more resistant to water-induced deactivation than monometallic Pt or Pd supported ones. The best performance reflecting in high and stable activity assisted by relatively low amount of evolved heat was exhibited by the Pd-rich bimetallic Pd-Pt(2:1)/SiO_2 catalyst [1].

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In situ sensibilization of amorphous TiO_2 by pre-synthesized colloidal CdS for photocatalytic 1,2,4-trichlorobenzene degradation

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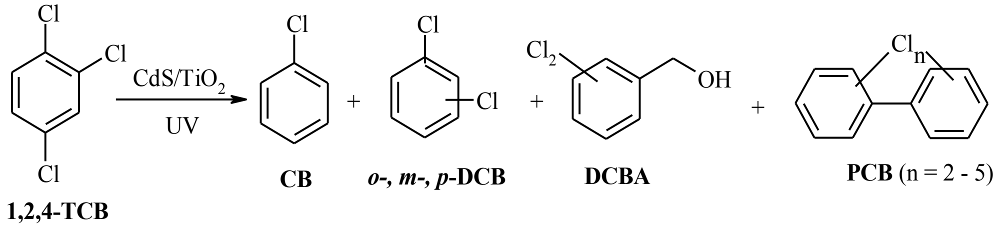
Various methods have been developed to reduce the band gap of TiO_2 via combing TiO_2 with quantum dots (QDs). However, the attainment of high activity and stability of hybrid QDs/TiO_2 is still a significant challenge since the poor interface contact between electronic systems of QDs and TiO_2. This drawback could be tackled to some extent through optimisation of the preparation technology. The present study suggests a simple hydrolysis route to *in situ* TiO_2 sensibilization by pre-synthesized CdS QDs, which play a role of crystal seeds, pre-planted in liquid titanium alkoxide, for the TiO_2 crystallization process [1]. The comprehensive investigation of the CdS/TiO_2 composite, carried out by X-ray diffraction, scanning electron microscopy, chemical composition, and photocatalytic dataset proved the successful sensitization of TiO_2 phase by CdS QDs. Catalytic activity measurements were conducted in the photodegradation processes of chloroarenes.

Chloroarenes are known to be the most toxic organic compounds contaminating environment [2]. 1,2,4-Trichlorobenzene (1,2,4-TCB) has been selected as a model compound for the study in conditions close to natural using a water/alcohol medium and UV radiation. Non-sensitized TiO_2 was established to play neither catalytic role. Conversely, CdS/TiO_2 composite particles consisting of CdS amorphous core and TiO_2 crystalline shell demonstrated high catalytic activity in the process of photodegradation of 1,2,4-TCB in aqueous MeOH. The main products of the photolytic degradation of 1,2,4-TCB were found to be chlorobenzene (CB), *m*-, *p*- and *o*-dichlorobenzenes (DCB), dichlorobenzyl alcohol (DCBA) and PCB congeners (Scheme 1).



Scheme 1. The main products of the photolytic degradation of 1,2,4-TCB

The CdS/TiO_2 composite exhibited stable catalytic properties in the concentration range of 10-50 mol.% The high CdS/TiO_2 catalytic properties are suggested to be due to the electronic structure of Cd atoms located on the CdS nanoparticles surface.

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Advantages of ultrasonic spray pyrolysis to prepare fine powder and supported catalysts for carbon nanofiber synthesis

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Nowadays, carbon nanomaterials (CNM) and carbon based hybrid materials are of great interest due to their high strength, thermal stability and electrical conductivity [1]. Such materials are known to have huge potential in the fields of reinforcement, energy applications, adsorption and catalysis. Commonly, CNM are obtained by means of catalytic chemical vapor deposition of various hydrocarbons (HCs). Adjustment of process conditions (temperature, HC nature and catalyst composition) allows one to synthesize CNM with controllable morphology. Nevertheless, synthesis of materials with uniform structure and narrow diameter distribution remains challenging task.

For this reason, we suggest using ultrasonic spray pyrolysis (USP) for catalyst preparation. This method is based on high frequency ultrasound treatment (1700 MHz) of precursor solution. Usually the process involves the following procedures: atomization of precursor solution (suspension) by ultrasonic nebulizer; drying of sprayed droplets of resulted aerosol in a preheated chamber; collection of formed particulate matter by a cyclone, filter bag or electric field precipitator.

In present research two different routes were investigated (fig. 1). First route was devoted to the synthesis of fine catalyst powder and consequently disperse carbon nanofibers. Secondly, hybrid materials representing CNM layer deposited on macrofibers (MF) were studied.

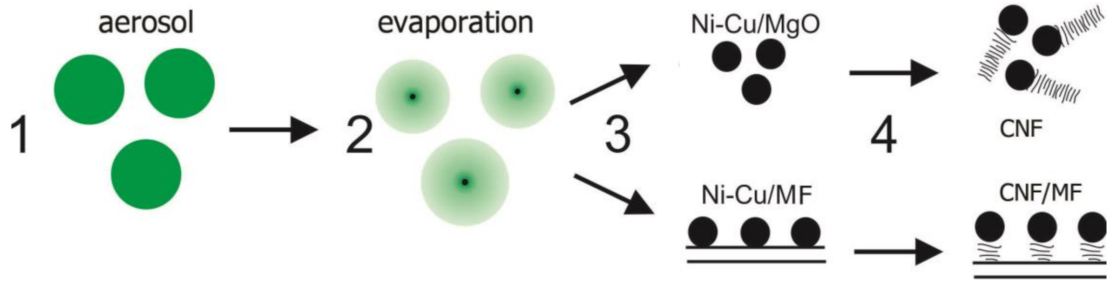

Fig. 1. Comprehensive scheme of routes to prepare CNF materials using USP

Peculiarities of active component formation in the course of USP process will be discussed in details. Catalyst morphology and particle size have been shown to depend on evaporator temperature, type of solvent and concentration of catalyst precursor. Additionally, CNM of different structural types were synthesized using the obtained USP-catalysts.

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PP-56

The structural determination of nanodispersed Pd, PdMe catalysts

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Today, great attention is attracted to development of highly effective approaches of converting renewable biomass into energy resources as biofuels. Some spirit compounds, such as ethanol, butanol, pentanol, glycerine, being biomass fermentation products, may be used as fuel components, both without any treatment and after catalytic converting, that provides production of more effective fuel components. The presented work is devoted to a study of the state and local structure of original nano-dispersed catalytic low-percentage systems PdMe (Me = Zn, Co, Mn, Ag), used for production of alkanes or olefins fractions C_4-C_{12+} which components of biofuels obtained from biomass fermentation products and others. Initial samples of catalysts were prepared by impregnation and zol-gel methods from original mono- and hetero-metallic precursors located on the oxide and carbon supports. All XANES and EXAFS spectra of the studied samples were recorded at Siberian Synchrotron and Terahertz Radiation Center (SSTRC, Novosibirsk). Genesis of the local structure of the studied catalytic nanosystems was characterized in detail. The interatomic distances and corresponded coordination numbers were revealed. All possible structural models were discussed. Relations between their catalytic properties, local structure distortions and state of metal components were demonstrated. It was found out that active components of all studied systems were highly dispersed onto the oxide and carbon support surfaces and strong interaction with the oxide supports took place, resulting in formation of mixed surface MeOx – support oxides. Additionally, the samples of catalysts were characterized by the TEM, EDX and XPS methods. The data obtained by all the methods are in a good agreement.

Acknowledgement. The work was done using the infrastructure of the Shared-Use Center “Siberian Synchrotron and Terahertz Radiation Center (SSTRC)” based on VEPP-3 of BINP SB RAS. This work was supported by RFBR (163350249, 163350248, 160301139, 163350250), SB RAS comprehensive program II.2P (Project 0305-2015-0018).

The structural study of gold catalytic nanosystems by XAFS spectroscopy method

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This work is devoted to a detailed structural study of the nanosized Au, AuMe stabilized forms located on oxide supports by XAFS spectroscopy method. It is a well known fact that metallic gold is most inert among the precious metals due to its electronic structure, nevertheless the nanosized Au, Au-Me forms located on oxide supports may be used as very active catalysts for numerous industrially important reactions. These systems are very promising for complex organic synthesis, selective isomerization reactions and for processes of environmental catalysts, such as, CO oxidation and selective conversion of secondary alcohols. Reliable analysis of the nature of gold forms is extremely important for design of new effective gold based catalysts for different industrial applications.

All XAFS spectra (Au-L_3 edge) of the studied samples were recorded at Siberian Synchrotron and Terahertz Radiation Center (SSTRC, Novosibirsk). Synthesis of low-percentage ~ 0.1-2 % Au, Au-Me samples was carried out under varying preparation methods (impregnation, deposition-precipitation with urea, direct ion exchange), calcination temperatures and activation methods. The state of metal components and the local Au structure arrangements of the prepared catalysts were studied. The Au-O, Au-Au, Au-Me interatomic distances and corresponded coordination numbers were established. All possible structural models were discussed. It was shown that different stabilized gold forms located on oxide supports were formed, most probably depending on a sample prehistory: Au(3+) cations, having octahedral oxygen surrounding and metallic Au-Au, Au-Me nanoparticles ~10-100 Å. Some correlations between catalytic activities and structural functional properties of the studied samples were shown. Additionally, samples of catalysts were characterized by the TEM, EDX, XPS, XRD methods. The data obtained by all the methods are in a good agreement.

Acknowledgement. The work was done using the infrastructure of the Shared-Use Center “Siberian Synchrotron and Terahertz Radiation Center (SSTRC)” based on VEPP-3 of BINP SB RAS. This work was supported by RFBR (163350249, 163350248, 160301139, 163350250), SB RAS comprehensive program II.2P (Project 0305-2015-0018).

PP-58

Synthesis and physical-chemical properties research of catalysts based on iron-containing layered oxides

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Perovskite-type layered oxides $GdFeO_3$, $GdSrFeO_4$ and $Gd_2SrFe_2O_7$ are Ruddlesden – Poppe phases. Compounds with similar structures are described by the general formula $A_{n+1}B_nO_{3n+1}$, where n = 1, 2, …, ∞ is the number of perovskite layers. These complex oxides were synthesized by sol-gel technology and their synthesis described in [1]. X-ray diffraction analysis, photon-correlation spectroscopy, and scanning electron microscopy showed that these complex oxides are in microcrystalline state, single-phase and a porous structure. The data obtained by BET method allowed us to conclude that the ferrites obtained by sol-gel technology have a low values of specific surface area, about 4-7,5 m^2/g. It was established by means of Mössbauer spectroscopy that iron in the samples of $GdFeO_3$ was in the form of Fe^{3+} ions localized in two types of fields with different symmetry, and that Fe^{4+} ions with oxygen vacancies coexisted in $GdSrFeO_4$ and $Gd_2SrFe_2O_7$ complex oxides along with Fe^{3+} ions localized in three types of fields with different symmetries. Currently, such compounds are intensively studied and find wide application as catalysts for high temperature catalytic processes such as dry reforming of methane (DRM). Because these complex oxides are able to maintain their catalytic and mechanical properties under the severe reaction medium.

After catalysis X-ray diffraction analysis was shown that investigation oxides didn't change its phase composition. Scanning electron microscopy of complex layered oxides $(Gd,Sr\ )_{n+1}Fe_nO_{3n+1}$ showed that there has been a noticeable change in the samples morphology in the catalytic process, particles form a rough surface structure. And for $GdFeO_3$ complex ferrite observed particle aggregation and the particles lose their porous structure. The Mössbauer spectroscopy data showed that the iron atoms state didn't changed after the DRM reaction. However, it has been shown the presence of only one iron form – Fe^{3+} for $Gd_2SrFe_2O_7$ sample unlike the original ferrite. Data energy dispersive x-ray spectroscopy (EDX) for the investigated samples after the catalytic reaction were shown the carbon presence on the sample surface (estimated about 5 %).

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PP-59

δ-Alumina supported cobalt catalysts promoted by ruthenium for Fischer-Tropsch synthesis

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Co-δAl_2O_3 catalyst precursor was synthesized using deposition by precipitation with urea. The promotion of dry Co-δAl_2O_3 catalyst with ruthenium was performed by incipient wetness impregnation using the aqueous solutions of *trans*-$Ru(NO)(NH_3)_2(NO_3)_3$ complex with Ru loading corresponding to 0.2, 0.5 and 1 wt.%. All catalysts were dried under IR lamp and calcined at 300-350 °C in Ar flow. The evolution of the phase composition, structure and surface composition of the samples were investigated by means of thermal analysis, XRD, FT-IR spectroscopy, XPS, TEM and SEM. Fischer-Tropsch synthesis was carried out at 190 °C, 2.1 MPa, using spherocylindrical catalyst particles of 2.5 mm in diameter and 4-5 mm in length in a single row fixed bed reactor. Before catalytic test catalysts were activated under the conditions ensuring the reduction of comparable fractions of metallic cobalt, in H_2 flow at the temperatures chosen from thermal analysis data.

It was shown that before the reduction, catalyst contain cobalt mainly in the spinel-like $Co_{3-x}Al_xO_4$ mixed oxide phase containing the impurity anions CO_3^{2-}, NO_3^-, OH^-. Ru-promoted catalysts contain also NO groups, which are produced during the Ru precursor thermolysis. Average sizes of $Co_{3-x}Al_xO_4$ crystallites are in a range of 5-10 nm. As ruthenium content in the catalyst increases upon reduction, the temperature of metallic phase formation decreases substantially (by more than 150 °C). The bimetallic ruthenium-cobalt metallic particles form during the reductive activation. In addition to Co-Ru particles, in 0.5-1.0 wt.% catalysts, a part of ruthenium forms individual ultradisperse metallic particles ca. 1 nm in size that are located on the surface of oxide support. The oxide layer decorating the surface of metallic cobalt particles is also strongly enriched with ruthenium. Catalytic results showed that selectivity of promoted catalysts for α-olefins and heavy hydrocarbons was higher in comparison with unpromoted catalysts, without a noticeable decrease in catalytic activity. Although the ruthenium-cobalt alloy segregates with enrichment of the surface with cobalt, the presence of ruthenium in the metallic particles and probably in the decorating oxide layer exerts a considerable effect on selectivity of the catalysts.

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PP-60

The investigation of $Cd_{1-x}Zn_xS$-based photocatalysts transformation during hydrothermal treatment

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Hydrogen seems to be an attractive alternative to traditional energy sources, but it exists in nature in the form of compounds with other elements. Water is an ideal hydrogen source. CdS is considered to be one of the most well-known semiconductor photocatalyst. The photocatalytic properties of CdS could be modified by mixing with wide band gap chalcogenide semiconductors such as ZnS [1].

In this study a series of $Cd_{0.3}Zn_{0.7}S$ photocatalysts were prepared by the coprecipitation method with subsequent hydrothermal treatment at different temperatures (80-160 °C). The best result equals to 6,7 μmol min^{-1} has been obtained using particles of $Cd_{0.3}Zn_{0.7}S$, treated at 120 °C. Further, NiS and Au were deposited on the surface of this sample. The activities of composite samples equal to 13,0 μmol min^{-1} and 14,9 μmol min^{-1} for NiS/$Cd_{0.3}Zn_{0.7}S$ and Au/$Cd_{0.3}Zn_{0.7}S$, respectively. The results of the kinetic measurements are presented in fig. 1.

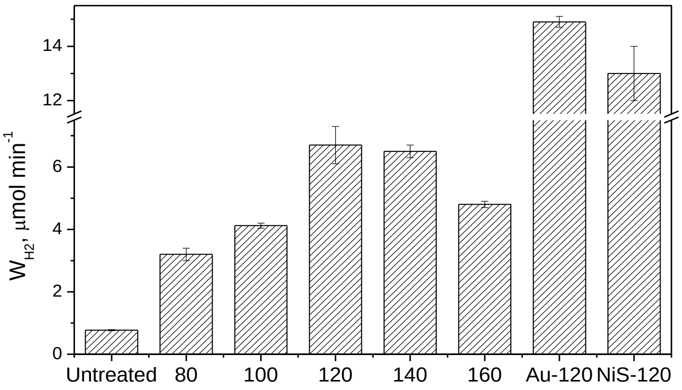

Fig. 1. Photocatalytic activities of synthesized samples

An improvement of H_2 evolution in the case of the treated samples likely caused by a change to a hexagonal lattice. It has been recognized early on, that the hexagonal structure is far more active than the cubic one [2]. With the addition of NiS and Au, photogenerated electrons in $Cd_{0.3}Zn_{0.7}S$ are migrated to the cocatalyst. Owing to the longer lifetime of photogenerated electrons, photocatalytic H_2 evolution rate is improved.

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PP-61

The catalyst transformations outside the catalytic cycles in cross-coupling reactions

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The whole set of palladium transformations occurring inside as well as outside the main catalytic cycle is the well-known feature of the cross-coupling reactions. This peculiarity led to the existence of several palladium forms that are able to interconvert during these catalytic reactions.

The establishing of the roles of different palladium forms in the cross-coupling reactions becomes possible using the simultaneous measurements of reaction kinetics by catalytic activity/reaction selectivity and spectroscopic characteristics of catalyst forms named *operando* study [1]. We use combined UV-VIS-spectroscopic study of the ligand-free catalytic systems in cross-coupling reactions with different substrates and simultaneous GC or GC-MS to establish the mechanisms of palladium transformations and their coupling with the main catalytic cycles of the reactions. Using this approach it has been demonstrated that applying Pd(II) salt as the catalyst precursor the formation of the Pd(0) molecular complexes being the active species proceeds as auto-catalytic process under the Mizoroki-Heck reaction using aryl halides as well as aromatic carboxylic anhydrides as the substrates. In addition, it has been established that this reaction is accompanied by the formation of $[PdX_4]^{2-}$ (where X^- are endogenous halide ions formed under substrate conversion or being the components of the catalytic system) species being the catalyst deactivation. The proceeding of similar catalyst deactivation processes has been shown by analogous approach in the Suzuki-Miyaura reactions with aryl iodides, while using aryl bromides in this reaction led to the disappearance of this deactivation route. In combination with the results of the study of differential selectivities of the Mizoroki-Heck and Suzuki-Miyaura reaction with different types of substrates such regularities point to the different types of the active species.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 16-29-10731.

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Influence of the structural features of PtCo (1:1) films on the electrochemical properties

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Influence of the structural features of the PtCo (1:1) films on the electrochemical properties

Numerous studies have demonstrated that alloying Pt with transition metals such as Co, Ni, Fe, increases its activity in the oxygen reduction reaction, whose slow kinetics is a serious hurdle in the development of efficient polymer electrolyte membrane fuel cells. Among binary alloys, the Pt–Co alloy has shown one of the most promising performance for the oxygen reduction reaction (ORR) [1]. Usually phase composition of the PtCo catalyst does not taken into account and so-called chemically disordered PtCo alloy phase is utilized for the study. However, under high temperature treatment disordered PtCo (1:1) phase can be transformed into chemically ordered $L1_0$ phase, which is based on the face centred cubic platinum lattice with tetragonal distortion along the c axis and which has a high magnetic anisotropy.

In the presented work, magnetron sputtering technique has been applied for the preparation of the PtCo (1:1) thin films. Variation of the single crystal substrates (MgO (001) and Al_2O_3 $(11\bar{2}0)$) and preparation conditions allowed to obtain cristallographically ordered samples with different degree of the chemical order.

Electrochemical study showed noticeably differences in the properties of the samples with different crystallographic planes and chemical order. Thus, PtCo (111) is less stable under electrochemical condition compare to the PtCo (001) sample. Significant influence of the chemical order on the activity in the oxygen reduction reaction has been found.

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PP-63

$NaWMn/SiO_2$ mixed oxide catalyst: thermochemistry of lattice oxygen

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Mixed $NaWMn/SiO_2$ oxide is a promising catalyst for ethylene production via oxidative coupling of methane (OCM). Unlike other efficient OCM catalysts, it contains two components (W and Mn) capable of changing their oxidation state in redox processes. Although its structural features and catalytic performance have been extensively studied, the nature of its catalytic activity is not yet well understood [1]. Recently we demonstrated that the system under study contains two forms of reactive lattice oxygen [2]. The first type can be considered as strongly-bonded; it can be reversibly removed by reduction with H_2 at temperature above 600 °C. The second one is more weakly bounded; it can be removed from the oxide by desorption in inert gas or in vacuum above 650 °C. The lifetime of this oxygen form at typical OCM temperatures (around 800 °C) exceeds the characteristic time of the steady-state catalytic reaction, and its presence in the catalyst substantially increases the rate of C_2-hyrocarbons formation if pulses of methane are supplied onto the oxygen-pretreated sample. Thus, it was concluded that the weakly-bonded oxygen is mainly responsible for methane activation in the steady-state conditions.

In the present work the in-situ differential scanning calorimetry (DSC) was employed to determine quantitative characteristics of both forms of active lattice oxygen.

The amount of 'weakly-bonded' oxygen (~56 mmole/g) and its binding energy with oxide lattice (~340 kJ/mole) were determined by re-oxidation of the sample after preliminary oxygen desorption. These numbers likely indicate that this type of oxygen adsorption/removal is associated with Mn(4+) <=> Mn(3+) transition.

The amount of 'strongly-bonded' oxygen (~443 mmole/g) and its binding energy (~420 kJ/mole) were determined by re-oxidation of the sample pre-reduced in hydrogen. They suggest that this form of active oxygen is associated with tungsten present in the sample. However, neither the particular ionic transition, nor the structural changes that occur during the removal of this form of oxygen can be determine from the existing experimental data without employing additional structure-sensitive techniques. Nevertheless, taking into account such a high value of oxygen binding energy one, can conclude that in the case of steady-state conditions (i.e. in the presence of O_2 in the gas phase, even in small concentrations), the strongly-bonded oxygen can play only a minor role in the catalytic process.

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PP-64

Interaction of a single oxygen atom with small palladium clusters

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Palladium is often used as an active component of catalysts applied for hydrogenation, dehydrogenation, oxidation, etc. [1]. Some *in situ* techniques, such as XPS [2] and FTIR [3], can be applied to study the active surface species and the catalyst state in the course of the catalytic reactions. However, because a catalytic process consists of many steps (diffusion, adsorption, elementary reactions), some problems sometimes arise concerning the experimental data interpretation. In this case, quantum chemical calculations can be useful.

In this work the density functional theory (DFT) calculations were performed to determine the optimized geometry and electronic energy of small Pd_n clusters (n = 1-8). This was done with different levels of theory (B3LYP, PBE0, B3P86, B3PW91). Then a single oxygen atom was added to various positions of the most stable Pd_n clusters (to the top, to the edge, to the flat and in the center of the cluster, where it was possible (n = 3 ÷8)), and the Pd_nO structure was optimized with different levels of theory. The lowest energy state for the Pd_nO structures was found. The 6-31+G* basis was used for oxygen, the LANL2DZ pseudo potential was used for palladium. The calculations were done using Gaussian 09.

The binding energy for Pd_n clusters as a function of n (number of atoms) reaches a plateau at n = 8, therefore, the Pd clusters of such a size can be already considered as a minimal appropriate model of Pd nanoparticles allowing one to perform the calculations in reasonable time with good convergence. The second energy difference calculations show that Pd_4, Pd_6 and Pd_8 clusters are the most stable that agrees very well with the literature [4, 5]. The energy of bonding between a single oxygen atom and the Pd_n clusters was also calculated. For a better correlation with experimental data, it is necessary to increase the cluster size, and this will be the subject of a future work.

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3-Steps Combined Plasma-Catalytic-Photocatalytic Oxidation of VOCs: The Effect of Plasma Current and Air Relative Humidity

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Photocatalysis is a great field of scientific and practical interest. One of the prospective usages of photocatalysis is oxidation of volatile organic compounds (VOC) [1]. On the one hand, the rate of photocatalytic oxidation (PCO) is relatively low due to charge carriers generation rate and adsorption capacity limitations. On the other hand, oxidation by means of nonthermal-plasma (NTP) is not limited by adsorption and allows one to reach high oxidation rates at room conditions. But strong disadvantage of this technique is pour conversion selectivity and generation of by-products (e.g. ozone). Combination of NTP with thermal catalysis and photocatalysis (PCP) can increase the efficiency of oxidation and decrease the concentration of by-products. Such increase was observed for toluene [2] and acetone [3] PCP oxidation with the $(CuO,MnO_2)/TiO_2$ and MnO_2/TiO_2 respectively. The effect is caused by decomposition of adsorbed pollutants and their partial oxidation products over the catalyst surface independently of the plasma by the generated ozone and reactive species. Moreover, the presence of plasma-generated ozone may enhance the PCO rate [4]. Therefore, the hybrid systems, which combine different techniques, are used now much more frequently than individual ones.

The combination of 3 individual techniques (NTP generated in corona discharge region, PCO over TiO_2 photocatalyst, and catalytic oxidation of gas mixture over ozone decomposition catalyst) was tested in oxidation of different VOCs.

The experimental results demonstrate that the oxidation by means of the combined approach provides:

- an increase of the acetone vapours oxidation rate by 28-50 % if to compared solely with the photocatalytic oxidation whereas the energy consumption increases only by 10 %;
- an increase of the synergetic effect with the increase of discharge current level;
- low values of carbon oxides formation rate under wide range of relative humidity.

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Transformations of the $Cd_{0.3}Zn_{0.7}S$ photocatalyst modified by nickel hydroxide and nickel sulphide during the photocatalytic hydrogen production in inorganic media

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The catalytic activity of semiconductor powders has aroused particular interest because of their possible application to the conversion and storage of solar energy as chemical energy [1]. From this point of view, the solid solution of cadmium sulphide and zinc sulphide with molar ratio 3:7 is known to be the most interesting material for further investigations [2]. In order to increase the photocatalytic activity of such material, it is modified by different cocatalysts such as $Ni(OH)_2$ and NiS [3].

The $Cd_{0.3}Zn_{0.7}S$ support was prepared by the method described in detail elsewhere [2]. The modified photocatalysts were labelled as NiOH-x where x was a calculated weight content of the deposited nickel hydroxide and prepared by the impregnation with nickel salt and following adding of sodium hydroxide. The photocatalytic activity of the synthesized samples was measured in the hydrogen production reaction from aqueous Na_2S/Na_2SO_3 solutions under visible light. The highest photocatalytic activity was 6.12 mmol h^{-1} g^{-1} for NiOH-0.06 sample after 3 h irradiation.

The transformations of the NiOH-x samples were studied by XRD and TEM methods. It was shown that the NiOH-x samples consisted of the support, $Ni(OH)_2$, NiS, and Ni_3S_2 phases. The XRD and TEM methods demonstrated that the aggregation of the support nanoparticles can be realized. The NiS phase was stable and didn't change the composition during the photocatalytic hydrogen evolution. The Ni_3S_2 phase could photoinducely transform to NiS [4]. The most interesting behavior was observed for nickel hydroxide. The highly dispersive particles of NiO were found after 3 h irradiation on the NiOH-0.06 sample by the TEM method. Probably, the nickel hydroxide phase was reduced to Ni^0 by the photoinduced electrons; the metallic nickel oxidized in air to the identified nickel oxide phase. However, the TEM analysis of the NiOH-5 photocatalyst after 3 h irradiation revealed only the NiS phase. Therefore, we can conclude that the rates of the photoinduced reduction and sulphurization processes defined the photocatalyst composition.

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PP-67

Self-activation of NiPd/$Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$ catalysts during autothermal reforming of methane

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To date Ni-based catalysts are the most common ones for methane reforming because of their high activity and low price [1]. Usually their reduction by H_2 before reaction is required for formation of Ni^o species working as active sites for methane reforming. However, Ni catalysts are often inclined to deactivation in the daily start-up and shut-down mode of methane reforming due to Ni re-oxidation and sintering [2]. To overcome this problem the modification of Ni catalysts by noble metals is applied. In this study the effect of Pd content and preparation mode on self-activation behaviour of NiPd/$Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$ catalysts during autothermal reforming (ATR) of methane was studied.

The sequential or combined impregnation methods were applied for the introduction of the active component into support. After drying the catalysts were calcined in air at 500 °C. Nominal contents of Ni and Pd metals were 10 wt. % Ni and 0-1.0 wt. % Pd. The ATR of CH_4 reaction was studied at a pressure 1 bar and a temperature 850 °C, with a feed composition $CH_4:H_2O:O_2:He = 1:1:0.75:2.5$, total flow rate 200 ml/min, catalyst loading 0.5 g and a quadrupole mass-spectrometric analyzer used for gas analysis [3].

It was shown that Ni/$Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$ catalyst used “as is” shows low performance: only 40 % methane conversion (X_{CH4}) and 3 % hydrogen yield (Y_{H2}). The pre-reduction of catalyst leads to its activation: $X_{CH4} = 100$ %, $Y_{H2} = 65$ %. However, the Ni catalyst shows deactivation with time on stream. The Pd introduction results in the high catalyst activity without pre-reduction, as well as in the suppression of catalyst deactivation. The self-activation behaviour of NiPd catalysts is maintained upon decreasing Pd content from 1 to 0.05 wt. %. At similar phase compositions of catalysts, differences in their functional properties correlate with Ni^{2+} reducibility. It was established that the sequential impregnation method should be preferentially used for active component loading into support matrix, which could be connected with particular features of Pd modifier distribution.

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Regularities of the formation of active component in the preparation and under reaction conditions on the Ga-Al-oxide-based catalysts dehydrogenation

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Two main types of compounds are typically used for the nonoxidative dehydrogenation of light paraffins: Pt-based and CrO_x-based catalysts. However, Pt-based catalysts have been having problems with coke deposits and the agglomeration of the platinum nanoparticles during the regeneration process or the dehydrogenation reaction [1]. Due to content of carcinogenic Cr^{6+} species, the CrO_x-based catalysts have been having environmental problems. Because of these reasons, the purpose of our work is to develop a new catalyst dehydrogenation with other elements. So using gallium oxide we have obtained promising results. Supported gallium oxide catalysts were prepared by impregnating the P-CTA-product of gibbsite (the mesoporous alumina) [2] with appropriate amount of aqueous solution of $Ga(NO_3)_3 \cdot 9H_2O$. The gallium content was varied from 1.5 to 9 wt. %. After drying the samples were calcined (T_{cal}) at 650-900 °C. The methods of low-temperature desorption N_2, NH_3-TPD, H_2-TPR, XRD, TG/DTA were used for the study of the catalysts. The dehydrogenation of isobutane was performed under atmospheric pressure at 560-580 °C and GHSV=445 h^{-1}. The results dehydrogenation at 580 °C are presented in Table 1. According to H_2-TPD date the gallium oxide in the composition of catalysts is reduced under reaction conditions and its content affects the displacement of hydrogen absorption peak.

Table 1 – Catalytic data of gallium oxide-based dehydrogenation catalysts

Catalyst	T_{cal}, °C	Yield of i-C_4H_8, mol. %	Conversion, mol. %	Selectivity, mol. %
9% Ga	650	31.5	54.6	57.7
6% Ga	700	30.6	46.2	66.3
6% Ga	800	28.2	38.1	73.9
6% Ga	900	17.3	22.2	78.0
3% Ga	650	27.4	42.0	65.2

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PP-69

The catalytic activity of fiberglass catalysts in the reaction of carbon dioxide reforming of methane by the process temperature

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Samples of the catalysts were prepared on the basis of fiberglass brand KT-11-TO, with stand temperature 1200 °C. The active catalyst components were deposited on the surface of the fiberglass matrix by "solution combustion" method [1]. Used vertically standing catalytic reactor with the top feeding the reaction mixture (CH_4 + CO_2). The activity of the catalysts was tested on-line using a gas chromatographic analysis method on the device "Chromos GH-1000" on packed columns filled with sorbents NaX (2 columns) and Porapak N (1 column). As the carrier gas He and Ar performed using a thermal conductivity detector.

The effect of temperature on the catalytic conversion process of the starting components (CH_4 and CO_2) and yield of the desired products (CO and H_2) for the catalysts that have in their composition MgO, NiO, Cr_2O_3 were investigated.

The maximum values of CH_4 and CO_2 conversion is observed at a temperature of 857 °C and = 87 % methane, 96 % carbon dioxide, respectively. The yields of hydrogen and carbon monoxide are increased at a temperature of 857 °C and reaches a maximum value. Yield H_2 – 35 %, CO – 42 %.

Dependences characterizing completeness of the reaction of carbon dioxide reforming of methane - $[H_2 + CO] / [CO_2 + H_2O]$ and $[H_2O] / [CO]$ and $[H_2] / [CO]$ were obtained. Also counted data for the formation of carbon deposits on the catalyst surface based on mass balance calculation.

Thus, it was found that increasing the reaction temperature of carbon dioxide reforming of methane leads to increased conversion of the starting components, increased yields of the desired products (CO and H_2) and a rather large coke formation.

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PP-70

Influence of superficial TiO_2 on the valent state, restorability and sizes of crystal grains of nickel in catalysts of hydroprocesses

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By valuable quality of titanium-oxide carriers for synthesis of NiMo catalysts of hydroprocesses is raise of dispersity of metals coating on them. In this work, we investigate a dimensional change of crystals of the metal nickel formed after restoration of nickel structures (4 % weight NiO) on various supporters (carriers). Nickel bring soakage on alumkaolin supporter (carrier) (AKB) and the supporter (carrier) inoculated TiO_2 by molecular coating AKB - TiO_2.

Results of research by methods of electronic spectroscopy of the valent state, the thermoprogrammed restoration and chemosorption of oxygen nickel containing systems and formations of the metal centres of nickel are presented.

It is shown that nickel oxide, coated on titanium dioxide in anatase form has three well enough divided maxima. Parameters of electronic spectra of the samples containing more 3 % NiO in the form of aggregates practically coincide with parameters of a phase of oxide of nickel, testifying to presence on a surface of three-dimensional aggregates of NiO. At an increase in temperature above 500 °C there is a removal of oxygen from the near-surface layer of nickel structures, bond Ni-O-Ti is broken off with restoration of hydroxyl covering on surface AKB-TiO_2 and formation of corpuscles of metal nickel dispersed on a supporter (carrier) surface. According to the data of electronic spectroscopy of diffuse reflection, predominating part NiO coated on AKB, is in the composition of superficial nickel-aluminum spinel. Nickel in structure superficial spinel on AKB is strongly connected with aluminum oxide and restored by hydrogen at temperature above 700 °C. At coating nickel oxide on surface AKB-TiO_2 and calcination at 550 °C, bond strength of ions of nickel with the inoculated carriers increases. It follows from displacement of a maximum of hydrogen absorption towards high temperatures. The size of nickel crystalline particles on the inoculated sample reaches to 9,7 nanometers, and on initial 15, 2 nanometers, it is probable owing to mutual protection of nickel oxides and the titanium from crystallization.

In case of NiMo catalysts, the restoration of transition metals proceeds under the multistage circuit. However, results on chemosorption O_2, testify about major dispersity Ni^0 in catalyst NiMo/AKB-TiO_2, in comparison with NiO/AKB.

Active state of cobalt catalysts formed in $NaBH_4$ reaction medium

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Catalytic hydrolysis of sodium borohydride ($NaBH_4$) is currently one of the best candidates for use in portable fuel cells because of safe generation of high purity hydrogen at ambient temperature. Cobalt catalysts have been shown to be a potential alternative to high cost noble metals in $NaBH_4$ hydrolysis [1]. There have been publications on the formation of a catalytically active cobalt-containing phase immediately in the $NaBH_4$ hydrolysis medium (*in situ*). The active state of cobalt catalysts is little studied. In this work we have studied the active state of cobalt catalysts formed in the hydride medium and effect high-temperature treatment on its physicochemical and catalytic properties.

It was shown that the molar ratio of elements in reduced catalyst is Co:B:O:H=3.2:1.5:1.4:1. Using TEM it was found that the forming nanosized particles of the active phase consist of an amorphous core and an oxygen-containing shell of amorphous cobalt borate. According to XPS, cobalt in the core is present mainly in the reduced state. In spite of its amorphous state, the catalyst showed a residual magnetization indicating the presence of small clusters of a ferromagnetic phase in formed core-shell nanoparticles. By using EXAFS it was possible to get an insight into the local environment of cobalt in the catalyst core. Thus in the ARDF curve there are peaks corresponding to Co-B (2.05 Å) and Co-Co (2.46 Å), the latter distance being close to that in metallic cobalt with a hexagonal lattice. After drying at 70 °C the changes in interatomic distances were insignificant while the coordination numbers increased both for Co-Co (2.7→3.3) and for Co-B (1.6→2.7) probably because of the removal of water or hydrogen from the first coordination sphere of cobalt. The EXAFS study was supplemented by an X-ray investigation which confirmed the presence of clusters with the shortest Co-Co distances of 2.5 Å. The cobalt clusters in the amorphous matrix are distributed in a regular fashion and separated from each other by distances of 5.8 Å. On the basis of the obtained results, a quantum-chemical model of the catalyst has been proposed for the first time which explains stabilization of ferromagnetic tetramers of cobalt within the amorphous boron-hydrogen matrix.

Analysis of the results obtained by EXAFS, magnetic susceptibility measurements, TEM, XRD and thermal analysis made it possible to determine the structural changes in amorphous cobalt catalysts upon their thermal treatment and to find out the influence of such changes on the catalytic activity towards sodium borohydride hydrolysis.

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PP-72

Selective catalytic hydrogenation of 2-methyl-3-butyn-2-ol for fine chemicals in micro capillary reactor

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Selective hydrogenation of the triple bond is an important class of chemical reactions for the production of pharmaceutical products and perfumes. The challenges in this type of reactions are to control selectivity in hydrogenation of poly-functional molecules, and avoid the possible risk of reaction runaway. In this work, the liquid-phase hydrogenation of the triple bond has been investigated in the micro capillary reactor. This technology represents a step forward compared to the existing technology of hydrogenation because it provides environmental safety, control of residence time and high rates of heat and mass transfer. Catalysts based on nanostructured oxide with embedded nanoparticles have been synthesized as a coating on the inner surface of the micro capillary reactor. The titania supported PdZn bimetallic catalysts with different composition [2, 3] have been tested in hydrogenation of 2-methyl-3-butyn-2-ol. The catalytic parameters were measured at different initial reactant concentrations, pressure temperatures and residence time. The concentration profiles were modelled using the Langmuir-Hinshelwood kinetics with competitive adsorption of organic species and dissociated hydrogen on the catalyst surface [4]. The considerable attention has been paid to the formation of active catalyst state under activation conditions. The investigation resulted in fundamental information on reactor performance for model reaction, evaluation of developed catalysts for hydrogenation reactions under the continuous flow conditions being used. The results demonstrate that the microcapillary reactor might be a promising technology to transfer conventional heterogeneous catalysis to flow regime.

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PP-73

Efficient Ni/NiOx Catalysts for the Hydrogen Electrode Reactions in Alkaline Medium

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For many years, electrocatalytic hydrogen evolution and hydrogen oxidation reactions (HOR/HER) have attracted strong research interest due to their fundamental and applied significance. The HOR/HER are the key processes in hydrogen-fed fuel cells and water electrolyzers. During the past 10 years an increasing interest in replacement of acidic electrolytes in these devices by alkaline medium is observed and stimulated by the development of new generation of anion exchange membranes [1]. The main advantage of alkaline electrolytes is the possibility to use non-noble metal catalysts, which are unstable in acid. Among these catalysts, Ni is perceived as the most promising candidate due to its relatively high activity in the HER, sufficient corrosion stability and low cost. However the activity of Ni in the HOR/HER, reported in the literature, may differ by nearly two orders of magnitude depending on the pretreatment conditions of the electrode [2]. Besides, recent studies [2-4] point out a notable influence of Ni oxide species (NiOx) on the surface of Ni on its activity in the HOR/HER.

In this work we have studied the HOR/HER over polycrystalline Ni disk electrode and electrodeposited Ni nanoparticles and showed that specific activity of Ni increases by more than 10 times, if partially oxidized Ni surface (Ni/NiOx) is formed under reaction conditions. The reasons for the enhancement effect is discussed with the help of microkinetic modeling, which provides very important information about the mechanism of the hydrogen electrode reactions. Electrochemical measurements have been done at various temperatures, allowing us to discuss the influence of temperature on the kinetics of the elementary reaction steps.

Prepared by electrodeposition technique Ni/XC-72 catalyst contains Ni nanoparticles with mean particles size around 10 nm homogeneously distributed over the surface of carbon support. In operando activated catalyst shows 10 and 5 times increase of its initial surface- and mass-weighted activities, respectively, being the most active catalyst for the HOR/HER in alkaline medium over platinum-group metal free catalysts studied up to now.

Acknowledgement. This work was supported by the RFBR project №16-33-00331 mol_a.

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PP-74

In situ XPS studies of kinetic hysteresis in methane oxidation over Pt and Rh catalysts

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Recently, we found that the activity and selectivity of the platinum catalysts in methane oxidation depends greatly on a way of achieving the steady state [1,2,3]. Using this hysteresis one can directly control the selectivity and activity of the platinum catalyst even with low initial activity, improve the conversion from 10 to 90 %.

To elucidate formation of active catalyst state under reaction conditions, we studied changes in oxidation state of the active component in real platinum and rhodium catalysts by *in-situ* X-ray photoelectron spectroscopy (XPS).

In-situ XPS experiments were carried out on a photoelectron spectrometer VGESCALAB "High Pressure" [4] equipped with a special high-pressure cell and a quadrupole mass spectrometer with two-stage differential pumping and high-precision mass flow-controllers. Experiments were conducted at constant methane concentration (partial pressure of about 0.008 mbar) with varying the O_2:CH_4 ratio in the range from 0.2:1 to 2:1.

Previous studies of the hysteresis were conducted in reactors at the atmospheric pressure. However, our *in-situ* XPS experiments showed the presence of similar kinetic hysteresis at low pressures. Study included testing possible catalytic activity of the alumina support and *in-situ* cell. It was shown that the pure support and *in-situ* cell were not active in the reaction. The experimental data showed that the activation in the reaction was associated with predominant formation of the metallic form, whereas oxidation of metal species was responsible for a less active state. The reaction mechanisms for explanation of these data are discussed.

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PP-75

Catalyst macroporosity in heavy oil hydroprocessing

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The choice of optimal porous structure provides significant opportunities for enhancing the activity of industrial catalysts [1]. In case of heavy oil refining industry, which performs the processing of complex macromolecular mixtures through multiple simultaneous reactions, a tunable porous structure is a powerful tool for controlling activity, selectivity and lifetime of the catalyst.

Our study, both theoretical and experimental, is focused on the development of novel porous catalysts for hydroprocessing of heavy oils, containing asphaltenes, metal chelates and heterocyclic compounds. The main approach is based on pore structure-directing templates consisting of polymeric monodisperse nano- and microspheres, which are able to tune textural properties of inorganic materials within wide limits. With the technique proposed one can adjust a specified pore size distribution and 3D-structured porosity with a characteristic pore size in the range from nanometers to micrometers. Catalyst supports based on meso-macroporous alumina with different porosities were prepared with the use of polystyrene microspheres (fig. 1). “Guard-type” catalyst, NiMo-alumina and NiMo-zeolite-alumina catalysts were tested in a three-stage hydroprocessing of crude heavy oil (360 sSt at 25 °C, 3.4 wt.% S, 110 wtppm Ni, 270 wtppm V). The templated catalysts were compared with the traditionally prepared materials in terms of catalyst activity in HDS and HDM reactions.

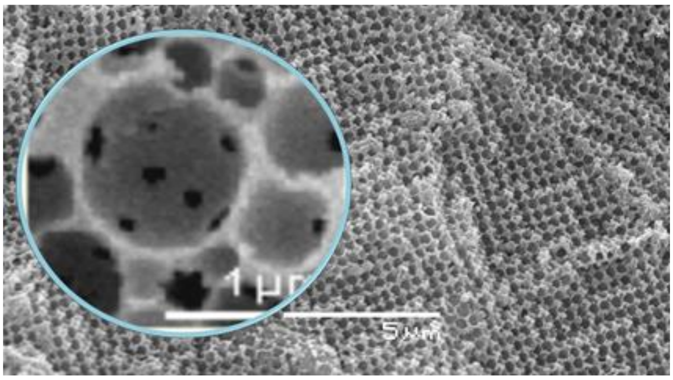

Fig. 1. SEM images of templated alumina

A theoretical study of substrate diffusion in porous materials was based on a model with random dense packing of uniform spheres forming mono- or bimodal pore structure with different porosities (fig. 2).

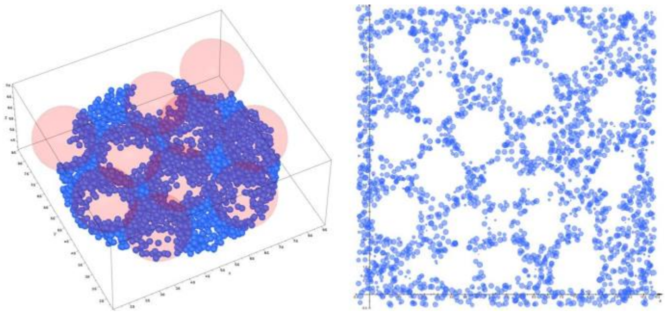

Fig. 2. Mathematical model of the material with bimodal porosity

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PP-76

Formation of metal-oxide nanocomposite catalysts from perovskites during reforming reactions

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Catalytic reforming of methane or oxygenates derived from biomass into syngas/hydrogen is an environment friendly process and now attracts a great attention. Ni-containing catalysts known as highly active ones in reforming reactions suffer from Ni sintering and strong coking leading to their rapid deactivation. These acute problems could be solved by using as precursors ABO_3 perovskites containing Ni, that provides a high Ni dispersion and oxidation of coke precursors due to high perovskite oxygen mobility [1].

In the present work, the catalysts formation from $LnFe_{1-x-y}Ni_yM_xO_{3-\delta}$ (Ln=La, Pr, Sm, Ce; M=Co, Ru; x=0÷0.4, y=0÷0.4) perovskites in the course of methane dry reforming (MDR) and ethanol steam reforming (ESR) was studied. The effect of the perovskite precursor composition on the catalysts genesis, their structural, morphological, redox features and catalytic performance has been studied by XRD, TEM with EDX, H_2-, CH_4-, EtOH-TPR, temperature-programmed MDR and ESR. It has been revealed that under reducing conditions of MDR or ESR perovskites are transformed into nanocomposites comprised of Ni-Fe(Ru, Co) alloy particles and LnO_x layers epitaxially bound with remaining Ln-Fe-O perovskite (Fig. 1). The type of Ln cation affects both Fe(Ru, Co) content in alloy particles and oxygen mobility/reactivity in perovskites. This demonstrates an important role played by remaining Ln-Fe-O phase in composites in MDR and ESR via activation of CO_2 (H_2O) and transfer of active oxygen-containing species to Ni-Fe(Ru, Co) alloy particles where they interact with carboneous fragments producing syngas. The most active and stable catalysts have been obtained from perovskites containing Ru due to optimal composition of formed Ni-Fe-Ru alloy. These catalysts provide a high syngas yield at 800 °C and 0.1-0.2 s contact time keeping their resistance to coking during more than 30 hours in the realistic reaction mixture: neither coke deposits nor fibers have been detected in discharged catalysts.

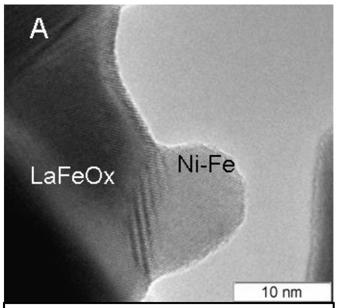

Fig. 1. TEM image of the catalyst formed from $LaFe_{0.7}Ni_{0.3}O_{3-\delta}$ during MDR

Acknowledgement. This work was supported by the BIOGO FP7 Project and by the Ministry of Education and Science of Russia.

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PP-77

Effect of the chemical nature of Me(III) cation on the structure, morphology and catalytic behavior of $CuMe_2O_4$ spinels in WGSR

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Mixed copper-containing spinel-type compounds $CuCr_1Fe_1O_4$, $CuCr_1Al_1O_4$ and $CuFe_1Al_1O_4$ were studied by means of XRD and HREM after treatment at 650 °C, activation in a hydrogen-containing medium at 270 °C, and participation in the low-temperature water gas shift reaction (WGSR). The effect of the chemical nature of Me^{3+} cation on the structural-morphological characteristics of oxide systems and their transformations in a reducing medium (under the activation and reaction conditions) was investigated. It was shown that the nature of Me^{3+} cation makes it possible to control the structural characteristics, particularly in the reduced state, and hence the catalytic properties in reactions with a reducing medium.

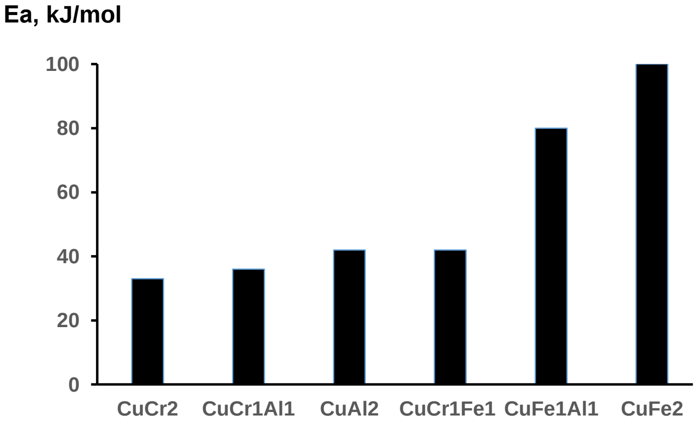

Figure. Dependence of activation energy of WGRS (150-240 °C) from the composition of $CuMe_2O_4$

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PP-78

Synthesis and catalytic properties of NASICON-type Cs-Co-Zr-phosphates for isobutanol conversion

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Solid-state ion conducting materials, also known as superionic or fast ion conductors, have been intensively developed. These materials can be used in solid-state electrochemical devices such as membranes [1] and catalysts [2]. The last years new catalysts family was developed on the base of complex phosphates of NASICON type, possessing the significant acidity and high thermal and phase stability. The basic structure of NASICON-phosphates is a framework that consists of PO_4-tetrahedra and ZrO_6-octahedra, along with cavities of various sizes and geometries (conducting channels) that can be filled by various polyvalent cations. The purpose of this study was to elucidate the effect of composition and hydrogen radiofrequency (RF) plasma treatments of the NASICON-type double and triple cobalt zirconium phosphate $Cs_{1-2x}Co_xZr_2(PO_4)_3$ with x=0,15; 0,25; 0,50 on its catalytic activity in vapor-phase reactions of isobutanol. All phosphates were prepared by sol-gel method. The prepared catalysts were characterized by X-ray diffraction analysis, XPS, DRIFTS of CO_2-adsorded, nitrogen adsorption measurements. The conversion of isobutanol was taken as a model reaction to measure the catalytic activity (acid and/or redox properties) of the prepared catalysts.

The activity of $Cs_{1-2x}Co_xZr_2(PO_4)_3$ in the dehydration and dehydrogenation of isobutanol depends on the surface properties and concentration of cobalt ions in the phosphates structure and on the RF plasma pretreatments.

The double phosphate was more selective for iso*b*utene, as the predominant dehydrated product. The triple phosphate catalysts exhibited higher activity towards isobutanol conversion. It was shown that RF plasma treatments are more effective for double phosphates, their catalytic activity increase in 2-4 times.

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PP-79

Ion-radical mechanism of converting some phenols to *p*-quinones by V-containing heteropoly acid solutions. Prospects to adjustment of reaction selectivity

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The influence of various reaction parameters on reaction time and product distribution was investigated in details during the catalytic oxidation of some dialkylphenols (2,3- and 2,6-dimethylphenols (Me_2Ps)) using molecular oxygen as oxidant and aqueous solutions of Keggin molybdovanadophosphoric heteropoly acids of the general formula $H_aP_zMo_yV_xO_b$ (HPA-x, x = 6–10) [1-2] as catalysts.

On the basis of kinetic and spectroscopic studies, an ion-radical mechanism involving dissociation of HPA-x in acidic medium to generate the active species VO_2^+ (equation (1)) and rapid stepwise oxidation of Me_2Ps to dimethyl-*p*-benzoquinones (Me_2BQs) by VO_2^+ with intermediate formation of several highly reactive particles was suggested (Figure 1).

$$(13\text{-}x)\ H_{3+x}PMo_{12-x}V^{V}_{x}O_{40} + 12\ H^+ \rightleftharpoons (12\text{-}x)\ H_{2+x}PMo_{13-x}V^{V}_{x-1}O_{40} + 12\ VO_2^+ + H_3PO_4 + 12\ H_2O \qquad (1)$$

It was found that ones of the important factors affecting the oxidation rate and product distribution are vanadium(V) content in the catalyst and its initial oxidation potential. When these values were higher, the yield of monomeric *p*-quinones was better. At low concentration of VO_2^+ the main oxidation by-products were identified as C=C-coupling dimers. Performing the oxidation in a two-phase system consisting of an aqueous solution of HPA-x with x of 8 or 10 in concentrations of 0.2-0.25 M and appropriate organic solvent, the best yields of the target quinones higher then 95 % were achieved at complete substrate conversion.

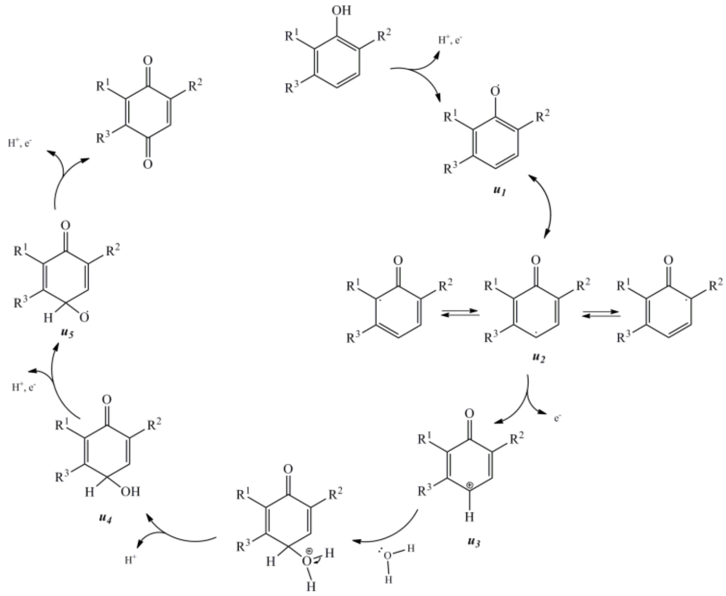

Figure 1. Mechanism of Me_2Ps oxidation to corresponding Me_2BQs in the presence of HPA-x aqueous solutions

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0008 for Boreskov Institute of Catalysis.

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Impact of the Pt Interparticle Distance in Pt/Al_2O_3 Catalysts Prepared by Laser Electrodispersion on Activity in CO Oxidation

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Catalytic activity of nanostructured metal catalysts strongly depends not only on a particle size but also on an average distance between metal particles [1]. This phenomenon is associated with interparticle and particle - support interactions. In addition, the electronic state of metal may depend on surface particle density [2] as well as on particle size [3]. Laser electrodispersion (LED) based on cascade fission of metal microdrops in laser torch plasma provides a unique opportunity to deposit size-selected metal nanoparticles only on the external support surface, and to study the influence of interparticle distance on structure and catalytic activity. In this work such investigation was performed using Pt/Al_2O_3 as the catalyst in CO total oxidation. The catalysts with 0.02-0.002 wt. % Pt loading were prepared by changing both a deposition time and an average granule size of alumina (0.08-0.7 mm). As the result the coating was varied in the range from 0.05 to 2.4 monolayers (ML). These catalysts were tested in CO oxidation by O_2 in the fixed-bed system (two cycles of gradual increase and decrease of reaction temperature) at pulse feeding of stoichiometric mixture (2 vol. % CO, 1 vol. % O_2, balance He).

TEM images demonstrated the uniform distribution of separated Pt particles or their small closely packed aggregates on the support even at high surface particle density. The mean Pt particle size was about 2 nm regardless of Pt loading. According to XPS data at high particle density on the support surface ($\geq$ 1 ML) the catalysts predominantly contain Pt^0 with $E_B(Pt4f_{7/2}) = 71.3$ eV. At low metal loading ($\leq$ 0.1 ML) platinum is oxidized to Pt^{2+} and Pt^{4+} with $E_B(Pt4f_{7/2})$ 72.5 and 75.2 eV, respectively, but the reduction of such forms proceeds under reaction conditions. During heating in the first catalytic test the catalysts comprising closely packed Pt^0 particles on the surface of large Al_2O_3 granules were more active than catalysts with the same Pt loading, but on smaller Al_2O_3 granules. However, in subsequent cycles the activity of catalysts on small Al_2O_3 granules strongly elevated. The temperature of 10 % CO conversion decreased from 350 to 210 °C for catalysts with optimal metal loading in the range of 1-0.25 ML. This effect may be due to the influence of the average distance between the particles on their redox and catalytic properties [4].

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PP-81

Formic acid decomposition over V-Ti oxide catalyst: mechanism and kinetics

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A detailed kinetic model for formic acid (HCOOH) decomposition on oxide vanadium-titanium (7.3 % V_2O_5/92.7 % TiO_2) catalyst has been developed based on transient kinetic studies and IR spectroscopy in situ. Formic acid decomposition to CO_2 (dehydrogenation) and to CO (dehydration) proceeds via different mechanistic routes. Dehydrogenation proceeds via the conventional ”formate’’ mechanism and include reversible dissociative adsorption of formic acid on vanadyl group V=O. The oxygen of the group acts as a proton acceptor whereas a vanadium cation is a formate anion stabilizer. Formate complexes can recombinate with protons and desorb in the form of formic acid or decompose to CO_2. Dehydration reaction follows a different mechanism. An interaction of the coordination unsaturated sites V^{+}-O^{-} with HCOOH leads to the synchronous cleavage of the C-OH and C-H bonds. Meanwhile the two OH hydroxyl groups are formed and CO molecule is evolved into gas phase. The path is completed by water desorption.

The rate constants and activation energies of elementary steps are calculated for a dehydrogenation and dehydration reactions. The rate-limited steps of the reaction are formate decomposition stage for dehydrogenation path (E_a = 60 kJ/mol) and water desorption stage for dehydration rout (E_a = 100 kJ/mol). The difference in the values of activation energies results in an increase of selectivity towards CO with reaction temperature elevation. Water inhibits formic acid decomposition. In the case the dehydrogenation, it connected with adsorption displacement of formates with water, whereas, in the case of dehydration, it is associated with an active centers blocking by adsorbed water. The developed kinetic model takes into account the water effect of both routs and satisfactorily describes the steady state reaction behavior.

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PP-82

Key Intermediates in Catalytic Systems for Di-, Oligo- and Polymerization of Olefins

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Electron magnetic resonance (EMR) and dynamic light scattering (DLS) technique are used to study the intermediate products of the catalytic systems of di- and oligomerization of olefins based on the azo-, azomethine complexes of Ni(II) and Co(II) with organoaluminium compounds. It was shown the formation of paramagnetic complexes of nickel(I) and cobalt(0, II), superpara- and ferromagnetic clusters of nickel and cobalt conditions, similar to catalytic. The stable and unstable at room temperature and below $T \leq 343$ K magnetic particles are identified.

In the table dynamic light scaterring data on the evolution of liquid phase catalytic system of dimerization of olefins based on the Ni(II) azomethine complex and Et_2AlCl are given. Perhaps this is the first direct experimental evidence for in situ detection of supramolecular structures in catalytic systems for di- and oligomerization of light olefins. It was shown that in situ, real time monitoring of catalytic system by DLS provides useful information regarding the formation, transformation of supra-molecular structures, dynamics of their size and concentration, allows to evaluate the size of particles in the nano-scale.

Table. DLS data on the catalytic system based on Ni(II) azometine complex

*Sample	DLS data							
	Diameter of particles in liquid system, nm						Span	Diffusion Coef, $E^{-11}m^2/s$
	Diameter for 10, 50, 90 % of particles			Median	Mean	Mode		
	10	50	90					
1,a**	1,9	2,4	2,9	2,4	2,4	2,4	0,41	3.56
1,b	1,8	2,2	2,8	2,2	2,2	2,3	0,43	3,79
1,c	1,2	1,7	2,2	1,7	1,7	1,8	0,58	5,02
2,a	562,1	785,5	1053,8	785.5	797,7	814,0	0,63	$1{,}08x10^{-2}$
2,b	538,8	804,6	1109,4	804,6	816,2	823,0	0,71	$1{,}05x10^{-2}$
2,c	528,0	794,3	1112,8	794,3	809,7	820,0	0,74	$1{,}07x10^{-2}$
3,a	504,0	837,5	1259,3	837,5	863,4	928,7	0,90	$1{,}01x10^{-2}$
3,b	631,3	916,2	1260,1	916,2	933,2	938,8	0,69	$0{,}93x10^{-2}$
3,c	539,0	869,8	1242,7	869,8	882,2	932,4	0,81	$0{,}98x10^{-2}$

*Sample 1 is the liquid solution of Ni(II) azomethine complex before the interaction with Et_2AlCl; 2,3 - the liquid solution of Ni(II) azomethine complex after reaction with Et_2AlCl in the absence and presence of ethylene, accordingly. **a,b,c are the each next measurements of the same system every 3 minutes.

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PP-83

Catalytic etching of platinum catalyst gauzes during ammonia oxidation

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Ammonia oxidation with air on platinum catalyst gauzes is widely used in chemical industry for synthesis of nitric acid. It is well known that during this process the gauzes undergo deep structural rearrangement of surface layers (catalytic etching) leading to the platinum loss and catalytic activity decrease. To determine the mechanism of the catalytic etching of platinum catalyst gauzes during the NH_3 oxidation, we studied in detail the surface microstructure of platinum catalyst gauzes used in ammonia oxidation. The platinum catalyst gauzes were made from a polycrystalline wire with d ≈ 82 μm with the chemical composition (in wt.%) 81 % Pt, 15 % Pd, 3.5 % Rh and 0.5 % Ru. A quartz laboratory flow reactor was used at the feed (ca. 10 % NH_3 in air) flow rate 880-890 l/h, the gauze temperature 1133 K and total pressure ca. 3.6 bar. The surface microstructure was studied using a scanning electron microscope JSM-6460 LV (Jeol).

A continuous corrosion layer on the front side of the first gauze relative to the gas flow after the treatment at T ≈ 1133 K for 50 h was observed after the SEM study. The SEM images demonstrate that the surface of the wire was significantly etched. The surface of the gauze was covered by a continuous corrosion layer consisting of crystalline agglomerates with the sizes 5-15 μm separated by deep voids with the width 1-10 μm. The agglomerates had different shapes, crystalline faceting and contained through pores with the diameter 1-5 μm. The obtained data indicate that the size of agglomerates on the front side of the gauze (5-15 μm) is close to that of grains observed on the back side (1-13 μm). This result seems to suggest that the etching develops in the course of gradual growth and transformation of the grains into crystalline agglomerates during the growth and merging of etching pits at the grain boundaries. Through pores with the size of 1-5 μm inside the agglomerates may be formed during merging of growing etching pits on the surface and in the bulk of the grains. The emergence and growth of the pits can be related to the reaction of ammonia molecules with oxygen atoms absorbed at the grain boundaries, dislocations and other surface defects. The reaction of gaseous NH_3 molecules with absorbed oxygen atoms with the formation of gaseous NO results in local overheating of the surface initiating the release of metal atoms to the surface. Intense release of metal atoms from pits at the grain boundaries forms extended voids between the grains. Metal atoms released from the defects quickly migrate over the grain surface and are gradually incorporated at the energetically most favorable sites. As a result, the grains are gradually reconstructed into faceted crystalline agglomerates with through pores. When these processes go on for a long time, a rough corrosion layer including crystalline agglomerates with through pores separated by deep extended void is formed.

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Influence of nitrogen-containing hydrocarbon compounds on the gas-phase oxidative desulfurization of DBT over B-Mo-modified CuZnAlO catalyst

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The main industrial method of treatment of diesel fractions is the process of hydrodesulfurization (HDS). To obtain required low sulfur diesel fuel (less than 300 ppm), the extraction of refractory compounds such as dibenzothiophene (DBT) and its alkyl derivatives, this method is technologically laborious. Recently the attention of researchers is turned to the development of methods of post-treatment of motor fuels after the HDS at mild conditions. A promising method of treatment may be a process of oxidative desulfurization of diesel fractions (ODS) by various oxidants, for example, hydrogen peroxide, ozone, and oxygen of the air, on different catalysts [1].

In previous works we have shown the possibility of gas-phase DBT oxidation to SO_2 by oxygen on B-Mo/CuZnAlO catalyst [2]. The authors of [3] showed that the presence of various nitrogen-containing compounds had an inhibitory effect on ODS with hydrogen peroxide. The information on nitrogen compounds effect on the ODS by air is absent. Thus, the aim of our work was to study the influence of nitrogen compounds in the gas-phase ODS of DBT on B-Mo/CuZnAlO catalyst. For the activity tests, model fuels based on toluene, containing 1000 ppm sulfur (DBT) and 300 ppm nitrogen (indole or carbazole), were prepared. The conditions of the tests were: $O_2/S=120$, GHSV=3000 h^{-1}, WHSV=6 h^{-1}, T=245-430 °C.

The transformation of nitrogen-containing compounds was observed already at 245 °C, and they were completely removed from model fuels at temperatures above 330 °C. However, the introduction of indole and carbazole led to a decrease of the activity in the oxidation of DBT at temperatures higher than 350 °C by 20 and 10 %, respectively. DTA-TG-MS analysis did not show accumulation of nitrogen compounds on the catalyst surface, but CHNS analysis detected nitrogen compounds in trace amounts. The GC-MS analysis of treated fuels did not show the formation of nitrogen or sulfur oxides, but it showed the formation of benzene and its alkyl and aryl derivatives as a result of alkylation and aromatic condensation of toluene.

It can be concluded that nitrogen compounds influence the gas-phase oxidative desulfurization of DBT over B-Mo/CuZnAlO catalyst at temperatures above 350 °C, decreasing the S removal in the following sequence: no nitrogen addition > carbazole > indole.

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PP-85

Pseudo in situ XPS analysis of real catalysts

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In this contribution we present our results of *pseudo in situ* XPS analysis of model and real Ni- and V-based catalysts. This approach bases on a treatment of the catalyst in a special high-pressure cell (HPC) of an X-ray photoelectron spectrometer with following transferring the catalyst under study, after cooling and pumping, to the analysing chamber without any contact with air. For the first time, similar experiments with Auger electron spectroscopy (AES) was described by G.A. Somorjai and co-workers forty years ago [1]. Afterwards, this approach was widely used in Surface Science experiments [2,3]. At present, it is more popular *in situ* and *operando* studies with application of different surface-sensitive methods such as XPS, XANES, FTIR, etc. Indeed, in this case it is possible to study not only the catalyst state, but also the main intermediates adsorbed on the catalyst surface [4]. However, *in situ* XPS, AES, and XANES measurements can be performed in the mbar pressure range whereas the real catalytic processes are conducted at pressure above 1 bar. As a result, the chemical state of the catalyst determined in these experiments can be different due to a slow rate of catalyst activation in vacuum. In recent years, we perform *pseudo in situ* XPS analysis of model and real catalysts using an X-ray photoelectron spectrometer (SPECS Surface Nano Analysis GmbH, Germany) equipped with HPC which allows us to treat the catalyst under study in different gas mixtures at pressure up to 5 bar in the temperature range between 20 and 450 °C. In some cases it is enough for obtaining adequate information about catalyst state [5-7].

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PP-86

New technology of soybean oil epoxidation

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Epoxidized soybean oil (ESO) is one of the best stabilizers of polymer chlorine content materials, including ones which are applied in food industry and medical technique. The base method of ESO production was soybean oil epoxidation with peroxyacetic acid or with the mixture of hydrogen peroxide and acetic acid. Usually the process is conducted in homogeneous phase, adding to reaction mass for this purpose homogenizer (acetone, dioxane and etc.).

To change these processes an epoxidation of soybean oil in heterogeneous phase was arised. In this case the removal of product is much easier. Epoxidation of soybean oil with the mixture of formic acid and hydrogen peroxide has become such a process.

Introduction of that process demands application of two-steps counterflow scheme, but allow to avoid additional components to ensure homogeneity of media for base reaction. As a result we have high purity of final product and possibility its application in medicine and food industry. Disadvantage of both methods is application either peracides or hydrogen peroxide. In last case in process without catalyst there are three phase: organic, water and gas phase.

The catalytic process of soybean oil epoxidation with nitrous oxide is studied.

There are only two phases in the process under study: liquid and gas phase N_2O. In this technology there is no separation stage of water phase-oil phase. Nitrous oxide as epoxidation agent has a number of advantages: more wide range operation conditions (tem-perature, pressure) high solubility in organic substances, easy removal from product, N_2O can be transported in liquefied state, provide high product selectivity.

This study is divided into two parts: a) Choice of catalyst and determine of epoxidation conditions. b) software development for experiment treatment. The experiments were carried out in batch reactor of ideal mixing. There were tested catalysts ZSM-5 type modified by elements Fe, B, Na [1-2]. The experiments were carried out at 313-353 ^{0}K, pressure 0.5-1.0 MPa. Nitrous oxide was diluted with helium by ratio 1:(3-5). The size of catalyst grains is varied from 0.1 mm to 10 mm. Experimental selectivity is 80-90 %.

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PP-87

Simulation of methanol dehydrogenation process in membrane reactors

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Methyl formate ($HCOOCH_3$), an industrially important compound in high demand for fine organic synthesis, is well known to be a key intermediate of C1-chemistry. However, the thermodynamics of methanol dehydrogenation is known to be quite unfavorable. High yield of the product can be achieved at high temperature only, when the side reactions are most accelerated.

The reactions of methanol dehydrogenation along with methyl formate decomposition to carbon monoxide and hydrogen were considered:

$2CH_3OH \Rightarrow CH_3OCHO + 2H_2$

$CH_3OCHO \Rightarrow 2CO + 2H_2$

The purpose of this research is an investigation of the process in catalytic membrane reactor, where the main attention should be focused on a shift of thermodynamic equilibrium due to the removal of hydrogen through the membrane into the external part of the reactor. Selective hydrogen removal allows one to shift the reaction equilibrium towards the desired products. On the other side, the highest values of methanol conversion could be reached in the case of the membrane reactor when the hydrogen oxidation reaction takes place in the shell side of the reactor. In this case, the dehydrogenation process could be realized at significantly lower temperatures as compared with conventional approaches.

In our research the effect of the additional oxidation upon the methanol conversion and methyl formate yield has been theoretically explored. The developed two-dimensional non-isothermal stationary reactor model takes into account the mass and energy balance equations with the appropriate boundary conditions for both tube and shell sides and for ceramic support layer. The developed model enables considering the volume change in the tube and shell sides of the reactor due to reaction stoichiometry and hydrogen diffusion through a membrane.

The kinetics parameters obtained for Cu/SiO_2 catalyst of methanol dehydrogenation was used for calculation [1]. The set of the process parameters was aimed to be optimized in order to obtain the highest methanol conversion along with reasonable selectivity towards methyl formate.

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PP-88

Polynuclear Mixed Valence Structures in Carbon Monoxide Oxidation on Co-Modified Zeolites

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Features of zeolite structure allow to stabilize the transition metal cation in unusual oxidation states and coordination environment and directionally to form the single-site catalysts based on polynuclear cationic oxo complexes [1,2]. Cobalt modified zeolites Co-ZSM-5 (SiO_2/Al_2O_3 = 55, 30) were prepared by the methods of solid–state ion exchange, incipient wetness impregnation and a combination of aqueous ion exchange and impregnation. The Co coordination geometry and electronic state was investigated by TEM, XPS and EXAFS/ XANES. New adsorption and catalytic sites resulting from the modifier introduction into the zeolite and its post reduction in CO atmosphere were detected by diffuse reflectance UV–vis spectroscopy (DRS) and infrared Fourier transform (DRIFT) spectroscopy, including the carbon monoxide adsorption technique. Catalytic activities of the materials were evaluated in CO oxidation by molecular oxygen. The reaction was carried out at atmospheric pressure in a quartz reactor tube in two systems - in a pulsed mode (CO : O_2 : He = 2 : 1 : 97 vol.%) and a flow type system (CO : O_2 : He = 1 : 1 : 98 vol.%).

According to XPS, X–ray spectroscopy and TEM in addition to isolated Co^{2+} ions cobalt oxide particles as Co_3O_4 or CoO and oxide-like structures $(Co_xO_y)^{n+}$ (n = 1, 2) containing Co^{3+} along with Co^{2+} species, are also may present on the surface of modified zeolites, especially at degree of exchange >100%. The ratio of the different types of cobalt species depends on the method of preparation. The low oxidation states of cobalt (Co^{+}) may perform on the surface of Co-containing zeolites in the course of the CO adsorption at RT, which is manifested in situ in the DRIFT spectra by the carbonyl complexes detected below 2140 cm^{-1}.

The obtained samples Co-ZSM-5 exhibit catalytic activity in CO oxidation with molecular oxygen at temperatures of 100-400 °C. The CO conversion reaches 100 % already at 200 °C. The relative concentration of Co^{+}/Co^{2+} redox couples which can be obtained on the zeolite surface after reduction by CO correlates with: i) amount of $(Co_xO_y)^{n+}$ (n = 1, 2) species containing Co^{3+} along with Co^{2+} cations and ii) catalytic activity of Co-zeolites in carbon monoxide oxidation by oxygen. Co-zeolites prepared by impregnation containing the highest amount of “oxide-like clusters” are much more readily reducible, and they are the best catalysts of CO oxidation.

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PP-89

Palladium species at stoichiometric and partially reduced ceria: a density functional study

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Ceria both in a pure form and with added metallic species is known to exhibit catalytic activity in many industrial processes. Peculiar catalytic properties of CeO_2 are attributed to the high mobility of its lattice oxygen. To investigate the effect of the extra- and intraframework palladium species on oxygen vacancy formation energy, $E_f(O_{vac})$, the theoretical DFT-GGA study on a model nanocluster $Ce_{21}O_{42}$ [1] was performed. The present results are critically analyzed together with our earlier data on ceria-supported silver species.

Our calculation shows that adsorption of Pd atom and Pd_4 cluster at a stoichiometric $Ce_{21}O_{42}$ model is the strongest upon interaction of metal moiety with two-coordinated O atoms at O_4-pocket of the (100) facet. The binding energies of Pd monomer and tetramer were calculated to be 4.08 and 3.47 eV, respectively, that is significantly higher than adsorption energies of Ag atom (2.17 eV) and Ag_4 cluster (2.86 eV) with analogous site of $Ce_{21}O_{42}$ nanoparticle. The electronic states of ceria-supported Pd atom and Pd_4 cluster are singlet and triplet, correspondingly. Similarly to Ag species reduction of cerium centers from oxidation state +4 to +3 is detected upon metal-oxide interaction.

The adsorption energies of Pd and Pd_4 species at a partially reduced ceria nanoparticle $Ce_{21}O_{41}$ are 2.91 and 3.04 eV. The lowering of binding energy can be explained by the reduced number of available for interaction with Pd particle oxygen centers from four to three. At the same time, the energy $E_f(O_{vac})$ is increased from 1.56 eV for metal-free $Ce_{21}O_{42}$ particle to 2.76 and 2.22 eV for Pd- and Pd_4-containing ceria species, respectively. Only minor growth of $E_f(O_{vac})$ to 1.66 eV is observed for $AgCe_{21}O_{42}$ system.

Interstitial substitution of a Ce center for a Pd atom at the (100) nanofacet also affects the mobility of lattice oxygen: the first O ion from O_4-pocket is depleted with energy gain of 0.23 eV resulting in $Ce_{20}PdO_{41}$ cluster. The energy of 1.70 eV is required for removal of second O lattice ion. In the most stable $Ce_{20}PdO_{40}$ structure Pd atom preserves its square-planar coordination.

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PP-90

Structural arrangement of the high active V_2O_5,WO_3/(Ce(Y)-TiO_2) catalysts in the reaction of selective catalytic reduction of NO with ammonia

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Diesel vehicles have attracted a large market share for its benefits as high power and good fuel economy. However, the emission of nitrogen oxides (NO_x) by diesel vehicles is harmful to the environment and human health. In order to eliminate NOx in many cases the harmful gas is cleaning by selective catalytic reduction (SCR) with ammonia to nitrogen using a V_2O_5/TiO_2 and V_2O_5,WO_3/TiO_2 catalysts. These catalysts are characterized by high activity in the temperature range 220-350 °C where nitrogen oxide conversion reaches 90-97 %, and the main reaction product is nitrogen. TiO_2 (anatase) is the most widely used as the support of the V_2O_5,WO_3/TiO_2 catalyst due to its better electron transfer and superior resistance to poisoning. Compared to the other supports, TiO_2 can remarkably improve the dispersion state of the VO_x species on the surface of catalysts. The main disadvantage of these catalysts is their low thermal stability. The activity dramatically and irrevocably degrades at temperatures above 350 °C. This is due to a change in the status of the active component (conversion of the high dispersed forms of vanadium to a coarse phase of V_2O_5), which is also accompanied by a phase transition of anatase to rutile.

The aim of this work is to study the structural arrangement of TiO_2 support modified by ceria and yttria additives and its effect on thermal stability and catalytic properties of high active supported vanadium catalyst for SCR NO with ammonia.

Synthesis of the support Me-TiO_2 where Me = Ce, Y was performed by incipient wetness impregnation of titanium dioxide (anatase) xerogel with an aqueous solution of cerium nitrate or yttrium nitrate salts followed by drying and heat treatment in air at 500-800 °C [1-2]. Obtained supports have higher specific surface area and more developed porous structure after thermal treatment, compared to pure TiO_2. It indicates on their more higher thermal stability compared to pure TiO_2 due to the formation of the nanocrystalline structure Ce-TiO_2 and Y-TiO_2 oxides.

Designed materials were used for the preparation of supported V_2O_5,WO_3/Ce(Y)-TiO_2 catalysts which were tested in the NO SCR reaction with ammonia in the presence of oxygen and water vapour. Catalysts have demonstrated a high catalytic activity and thermal stability up to the reaction temperature of 500 °C providing almost complete cleaning from NO.

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EPR study of electron-acceptor sites during catalytic dehydrochlorination of 1-chlorobutane

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One of the most intriguing properties of many heterogeneous acid catalysts is their ability to generate spontaneously organic radical cations upon adsorption of aromatic electron donors. ZSM-5 zeolites and sulfated zirconia materials possessing exceptionally strong electron-acceptor sites capable of ionizing compounds with very high ionization potentials, such as benzene (IP = 9.2 eV) [1]. The existence of weaker electron-acceptor sites with electron affinities ~ 7 eV in large quantities on the surface of many conventional oxides is no less remarkable. Electron-acceptor sites of different strength can be characterized using aromatic probes with different ionization potentials [1, 2]

Sulfated Al_2O_3 and ZrO_2 samples were studied in catalytic dehydrochlorination of 1-chlorobutane. The samples were placed in an EPR sample tube, activated in an argon flow for 1 h at the reaction temperature, and subjected to reaction with 1-chlorobutane. 1-Chlorobutane conversion to a mixture of butenes was monitored by gas chromatography. After the reaction was carried out for the desired time, the sample was quickly cooled down to room temperature and filled with a 2×10^{-2} M solution of perylene in toluene. The concentration of electron-acceptor sites was determined by integration of the EPR spectra registered immediately after the spin probe adsorption and after additional heating at 80 °C for 18 h.

Samples of pure and sulfated Al_2O_3 and ZrO_2 are characterized by substantial concentrations of electron-acceptor sites depending on the concentration of doped sulfates. The catalytic activity of pure Al_2O_3 and ZrO_2 and the concentration of electron-acceptor sites increased during the first 20 min on stream due to the surface chlorination that is known to increase the concentration of electron-acceptor sites. Activity of sulfated samples was higher initially and it is in good agreement with higher concentration of electron-acceptor sites. And their activity gradually decreased during the reaction reaching values similar to those close on pure samples. A good correlation was observed between the catalytic activity in dehydrochlorination of 1-chlorobutane and the concentration of weak electron-acceptor sites.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 16-33-00267 mol_a.

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PP-92

Specific surface area of the frame bulk porous material with the controllable geometrical parameters of structure and surface nanolayer

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The one/multi component frame bulk porous material with holes uniformly allocated on all surface is considered in report. Such material may be useful in chemical or electrochemical processes with participation and formation of the gaseous chemical compounds and requires the gas/liquid permeability of solid state material. The substantial surface area of material may be available for reaction (catalytic, electrochemichal or others) and it may be achieved also the better material's properties (corrosion resistance, mechanical stability, others). The material modification can be realized by precise physical/chemical methods (for instance, chemical or electrochemical etching, laser technology, lithography). It was calculated [1] that the material's specific surface area (thickness h and density ρ) with equidistant cylindrical holes (radius r) net is equal (Eq. 1, Figure 1):

$(\mathbf{S_1})_{\mathbf{spec}} = 2/\rho*[1/h + (\pi/(9 - \pi))/r] \sim 2/\rho*(1/h + 0.536/r)$.

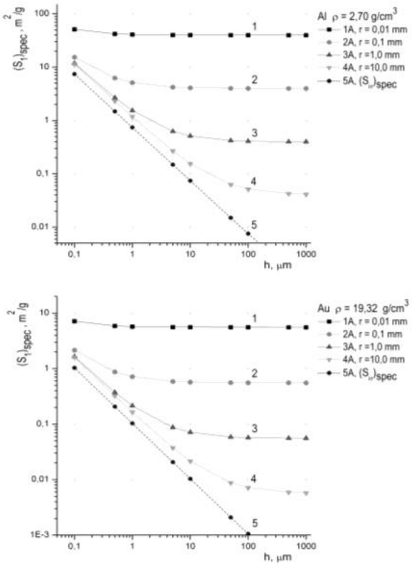

Figure 1 a, b

The relation of the specific surface area of the material with equidistant cylindrical holes net to the initial specific surface area of the material without holes is expressed by (Eq. 2):

$(\mathbf{S1})_{\mathbf{spec}}/(\mathbf{Sin})_{\mathbf{spec}} = 1 + \pi/(9 - \pi)*h/r \sim 1 + 0.536\ h/r$.

It has been also considered the frame bulk porous material with deposited nanolayer (submonolayer, monolayer or multilayer) that may be described by (Eq. 3): $(\mathbf{S1})\mathbf{d}/\mathbf{Sin} = \mathbf{S_1}/\mathbf{Sin}\ *(1 + \pi*N_d)$,

where $(\mathbf{S1})\mathbf{d}/\mathbf{Sin}$ is the relation of the result surface area of the bulk porous material with nanolayer to the initial surface area of the material without holes and nanolayer; $\mathbf{S_1}/\mathbf{Sin}$ - the relation of the result surface area of the bulk porous material without nanolayer to the initial material' surface area without holes and nanolayer; $\mathbf{Nd}$ – monolayers number. If the particles in the layer occupy the part D of the material surface area then the relation $(\mathbf{S1})\mathbf{d}/\mathbf{Sin}$ is expressed in (Eq. 4): $(\mathbf{S1})\mathbf{d}/\mathbf{Sin} = \mathbf{S_1}/\mathbf{Sin} * (1 + 4D)$;

$(\mathbf{S1})\mathbf{d}/\mathbf{Sin} = \mathbf{S_1}/\mathbf{Sin} * 1.4$, for $D = 0.1$; $(\mathbf{S1})\mathbf{d}/\mathbf{Sin} = \mathbf{S_1}/\mathbf{Sin} * 1.8$, for $D = 0.2$;

$(\mathbf{S1})\mathbf{d}/\mathbf{Sin} = \mathbf{S_1}/\mathbf{Sin} * 2.6$, for $D = 0.4$; $(\mathbf{S1})\mathbf{d}/\mathbf{Sin} = \mathbf{S_1}/\mathbf{Sin} * 3.4$ for $D = 0.6$.

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PP-93

Structural features of the gold nanolayer on the glass surface modified by surface ion exchange and chemical etching

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Key words: 1 – glass, 2 – ion exchange, 3 – chemical etching, 4 - X-ray structure analysis

The research data are related to X-ray structure analysis of the gold nanolayers (50, 100 and 200 nm thick) on glass surface modified by the surface ion exchange, chemical etching or by treatment combining two indicated above methods. The soda lime silica glass has been modified by the special Surface Ion Exchange Paste (SIEP) [1-3]. Na^+/Li^+ ion exchange with SIEP has next stages: glass surface degreasing and washing; the SIEP laying on the glass surface; thermal treatment at ~ 300 °C (15 – 20 min.); washing with running water. The chemical etching of glass have been carried out with the composition containing hydrofluoric acid [4]. The surface morphology has been observed by the SEM JSM-6460 (Jeol, Japan); the gold nanolayers were deposed by special device JVC-1600 (Jeol, Japan). X-ray data have been measured with diffractometer D8 Advance (with CuKα radiation) and one-dimensional detector Lynx–Eye with nickel filter. The range of the measurement was $2\theta = 10 – 120°$ with step 0,02° and acquisition interval 35,4°. The program Topas 4.2 (Bruker AXS, Germany) and initial structural data of inorganic base ICSD, FIZ Karlsruhe, Germany have been used.

X-ray data analysis allows make conclusion that the surface modification of the soda lime silica glass by the surface ion exchange and chemical etching have a substantial influence upon the size of gold crystal grains (Figure 1). Gold crystal grains have elongated shape in direction <111>. The increase of the gold nanolayer thickness leads to decreasing of the crystal grains size. The least size have been related to gold nanolayer 200 nm thick on glass surface modified by combined method indicated above: in direction <111> average calculated grains size is ~ 14.7 nm; grains size averaged in directions <200>, <220> and <311> is ~ 6.8 nm.

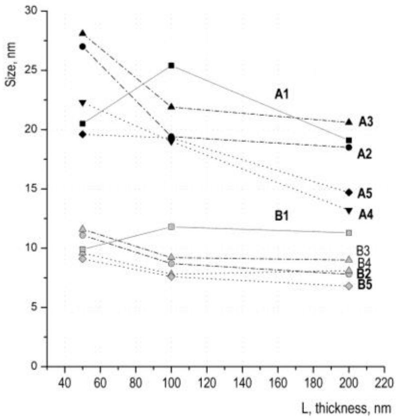

Figure1. Size of gold crystal grains in dependence on the gold nanolayer thickness

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PP-94

Subsurface (Dissolved) Oxygen Atoms in Supported Pt Particles As a Possible Active Species in Oxidation Catalysis

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The weaker is bonding to a catalyst of atomic oxygen participating in the catalytic reaction, the higher is activity of the catalyst provided that the reaction proceeds following a stepwise mechanism [1]. With molecular oxygen as an oxidant, O=O bond breaks (bond energy of ~500 kJ/mol) only in the case of formation of a strong bonds between the oxygen atoms and catalyst. When NO_2 molecules act as oxidant, the breaking energy of ON–O bond is much smaller (~350 kJ/mol) allowing to expect formation of oxygen atoms that bond to the catalyst weaker and, therefore, possess higher activity.

Using XPS, we investigated reactions of NO_2 with platinum particles deposited on oxide supports (Al_2O_3, SiO_2, TiO_2, ZrO_2) and carbon. Samples Pt/oxide were prepared in a chamber of XPS spectrometer in the form of thin films of supporting oxides on a substrate made of metallic plate or foil, with Pt particles evaporated on the support surface in vacuum. A HOPG single crystal served as the support for the Pt/C samples. According to TEM and STM, Pt particles were of ~2-5 nm in size. NO_2 was obtained by thermal decomposition of lead nitrate in vacuum.

When NO_2 reacts with Pt/oxide systems, various oxygen species on Pt particles were obtained: the subsurface (or dissolved) oxygen O_{sub}, anionic oxygen in surface oxides PtO and PtO_2. It is found that O_{sub} has an improved reactivity towards hydrogen compared with that of anionic oxygen. The interaction of platinum particles with molecular oxygen under identical conditions does not form O_{sub} and platinum oxides. Once NO_2 reacts with Pt/HOPG, only platinum oxides PtO and PtO_2 are produced. The lack of subsurface oxygen is assumed to be due to its high reactivity, which allows it to oxidize carbon at the Pt particles – HOPG interface, that is evidenced by changes observed in the C 1*s* and O 1*s* spectra.

The prospects of NO_2 use in low-temperature oxidation catalysis are discussed.

Acknowledgement. The work was supported by the Russian Science Foundation, grant 14-23-00146p.

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PP-95

Reactivity of oxygen species stabilized in Pt/MeOx systems prepared by RF-plasma

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The highly oxidized metal nanostructures have attracted attention due to their potential application as new electrode materials, supercapacitors, energy conversion devices, etc. These oxidized species can also be considered as active centres of catalysts in different oxidation reactions. Also, there is a number of data indicating the great influence of support chemical nature to the properties of oxidized particles. Thus, the development of the preparation methods of highly oxidized nanoparticles supported on different materials and investigation of their redox properties are of great interest. In this work the highly oxidized platinum nanoparticles were prepared by the radio-frequency (RF) sputtering of metallic electrodes in oxygen atmosphere. Two types of supports were used: stable Ta_2O_5 oxide and CeO_2 as a support with expressed redox Ce^{4+}/Ce^{3+} properties. The electronic properties of the oxidized species, their thermal stability and reactivity in CO oxidation reaction were studied using X-ray photoelectron spectroscopy (XPS). The particles size and their structural properties were analyzed by the Transmission electron microscopy (TEM).

The experiments were performed in the high vacuum conditions in the chamber of a VG ESCALAB HP spectrometer. The Ta_2O_5 oxide film grown on tantalum foil and CeO_2 powder pellet were used as supports. For TEM analysis the nanoparticles were sputtered on a copper grid covered with carbon film and immediately transferred to the microscope chamber.

According to the TEM data the RF-sputtering resulted in a formation of small Pt nanoparticles not more than 3 nm in size with the narrow size distribution. The increase of the coverage led to the particles agglomeration with formation of dendrite-like structures that comprise a large number of structural defects: grain boundaries, twins, stacking faults. The XPS spectra of the oxidized nanoparticles allowed to trace the formation of the Pt^{4+} species with $E_b(Pt4f_{7/2})$ = 74.0 eV and 74.5 eV on Ta_2O_5 and CeO_2 respectively. The difference in E_b could be attributed to the PtO_2 nanoparticles formed on Ta_2O_5 surface vs $Pt^{4+}CeO_2$ solid solution. The temperature increase induced transition $Pt^{4+} \rightarrow Pt^{2+} \rightarrow Pt^0$. It take place at 400- 425 K in case of Ta_2O_5 and >500 K in case of CeO_2 supports. It was shown that reactivity of oxygen in CO oxidation was higher substantially for PtO_x/CeO_2 than for PtO_2/Ta_2O_5 systems. The difference in thermostability and reactivity towards CO $Pt^{4+}CeO_2$ is attributed to the strong PtO_2 interaction with CeO_2, while on Ta_2O_5 PtO_2 nanoparticles stay individually.

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PP-96

Single-atom Pd-Ag catalyst for alkyne hydrogenation

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A single-atom catalysts (SACs) paradigm was originally proposed in 2013 and nowadays rapidly developing for industrial and laboratory practice[1]. SAC is cost-effective thermodynamically stable bimetallic system with single atom metal anchored to metal oxides or metal surfaces[2,3]. The latter is usually a composition with trace amount of active host metal isolated by the atoms of second (usually inactive) one. Supported SACs are ideal for the alkyne hydrogenation due to the possibility of effective elimination the multi-bonded adsorption of acetylenic compounds giving optimum selectivity in alkene formation[4]. In this research we study a structure, properties and performance of Pd-Ag nanoalloy single-atom catalyst in liquid-phase alkyne hydrogenation. The catalyst was supported from $PdAg_2(OAc)_4(HOAc)_4$ heterobimetallic complex (Pd:Ag ratio 1:2) onto $\alpha-Al_2O_3$. Detailed characterization was performed by FTIR-CO, TPR, and HR-TEM methods. Analysis of experimental data revealed the formation of bimetallic PdAg particles with the size ~ 10-20 nm in $PdAg_2/\alpha\text{-}Al_2O_3$. It is important that Pd exists as single atoms isolated by Ag on the surface of PdAg particles due to significant surface enrichment in Ag. Catalytic properties of PdAg SAC have been studied in the hydrogenation of diphenylacetylene (DPA) and phenylacetylene (PA) using commercial Lindlar catalyst as a reference. It was found that in DPA and PA hydrogenation PdAg SAC exhibit a high selectivity identical to that of the Lindlar catalyst. As a result of Pd modification with Ag the second stage of the hydrogenation (undesired conversion of target olefin to alkane) slows down considerably, making kinetic characteristics of the catalyst favourable for the effective control of both hydrogenation internal and terminal alkynes. This makes supported PdAg SAC a very promising alternative to Lindlar's.

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PP-97

Investigation of the stability of Mo/HZSM-5 catalysts with various Mo:Al ratios for non-oxidative conversion of methane

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The process for converting methane to aromatic hydrocarbons under non-oxidizing conditions is of considerable interest as a promising method of natural and associated petroleum gases recovery. Effective catalysts for this process are high-silica ZSM-5 zeolites modified with transition metal ions. Bifunctional properties of these catalysts are due to both acid sites of the zeolite itself and Mo-containing sites [1]. The aim of this work is to study the effect of the Mo:Al ratio in the catalyst systems prepared using zeolites with different silica module (M=16-80) and the nanoscale Mo powder (NSP) on their activity and stability in the course of non-oxidative conversion of methane into aromatic hydrocarbons.

Mo/ZSM-5 catalysts were prepared via solid-phase synthesis by mechanically mixing the H-form zeolites with a nanosized molybdenum powder. The catalytic activity of the samples was investigated in a laboratory flow setup at 750 °C and the feed space velocity of methane 1000 h^{-1}.

Our previous investigations on the process of methane conversion over Mo-containing zeolites with silica modulus 40 showed that the highest activity and stability were exhibited by the catalyst containing 4.0 % Mo nanopowder with the Mo:Al ratio being equal to 1:2. It was therefore of interest to investigate the influence of Mo:Al ratio in the catalysts prepared using zeolites with different silica moduli to achieve the Mo:Al ratio 1:2.

The tests of catalysts containing 4.0 % Mo showed that the lowest activity in the course of methane conversion was exhibited by Mo-containing zeolites with silica moduli 16 and 80. The highest stability during the whole reaction cycle was exhibited by the sample with M=40.

The tests for Mo-containing zeolites whose Mo:Al ratio was 1:2 have shown that it was the large amount of Mo nanopowder (8.6 %) in the zeolite with a low silica modulus (M=16) which resulted in a sharp drop in its catalytic activity and stability. The catalysts with the silica moduli 30 and 40 exhibited close values of methane conversion during the first 140 minutes. With the silicate zeolite modulus increasing to 60 or 80 the activity and stability of Mo-containing catalysts in the course of methane conversion are lower as compared with the catalysts prepared on basis of zeolites with the silica moduli 30 and 40.

Thus, the results obtained suggest that the Mo:Al ratio in Mo-containing zeolite systems is of great importance for the formation of active sites of a methane molecule activation and hence for manufacturing the most selective and stable catalysts for the process of methane dehydroaromatization.

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PP-98

Fibrous alumina – a new type of catalyst support

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Abatement of waste gases containing harmful VOCs is an environmentally important task, benzene, toluene and xylenes being among the most emitted VOCs. One of the most efficient and economically feasible VOC removal technologies is catalytic combustion [1-3], which can operate with dilute VOCs effluent streams and at much lower temperatures and residence times than non-catalytic thermal incineration. Recent works reported oxidative destruction of aromatics over noble metals, vanadium and copper supported on alumina [2,3].

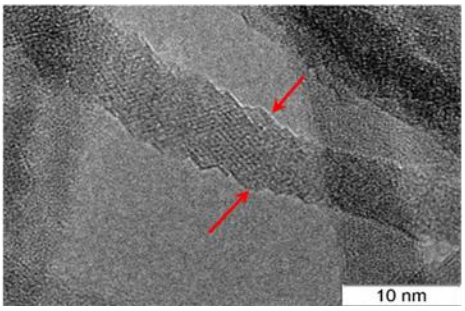

Fig. 1. HRTEM image of NAFEN

Fibrous alumina (trademark NAFEN) [4] is a new material differing from conventional Al_2O_3 in both structure and surface properties. It is manufactured under controlled oxidation of aluminium melt at oxygen deficit. Alumina nanofibers (θ phase) 10 nm in diameter (S_{BET}=150 m^2/g) have a highly defect tooth-like surface structure with a number of low-coordinative sites (Fig. 1). According to IRS data, nanofiber's surface is characterized by rather strong basicity (PA = 920 kJ/mol). At the same time, many catalytic processes require reduced basicity and presence of surface acid sites. It was shown that basic sites can be suppressed to form strong Broensted acid sites via alumina modification with mineral acids (H_2SO_4, HF) or TEOS. Such modification creates up to 120 μmol/g of strong BAS with a strength (PA = 1150-1170 kJ/mol) close to that of high-silica zeolites.

Copper deposition on fibrous alumina is accompanied by its strong interaction with support to form Cu species of atomic dispersion without bulk metal or oxide. Like in zeolites, catalyst evacuation and heating leads to copper reduction to Cu(I). According to DRIFTS data, copper state changes after modification of alumina surface.

Cu/NAFEN catalysts were tested in oxidative destruction of benzene at 250-350 °C with low and high oxygen content, and they were more active and stable compared with conventional Cu/alumina ones [2,3]. It was also found that modifier nature affects catalytic performance. Indeed, electron affinity of alumina modifiers increases in the range $SiO_2<F^-<SO_4^{2-}$; and in this range catalyst activity declines monotonously, while CO/CO_2 ratio rises from 0.6 to 30. Hence, such catalysts can be also promising in reactions of partial oxidation.

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PP-99

Oxidation and corrosion of polycrystalline palladium during CO oxidation

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Investigation of the catalytic CO oxidation by oxygen on platinum metals is interesting both for determining mechanisms of heterogeneous catalytic reactions and for protection of the environment from harmful exhausts of automobile engines, which contain a lot of CO that is very dangerous for the environment. Today palladium is widely used for preparing catalysts for converters of automobile exhaust gases because both Pd and PdO are more active than other platinum metals in catalytic oxidation reactions in the O_2 excess. The goal of this investigation was to study the microstructure of the palladium surface during the catalytic CO oxidation by oxygen at T = 800-1000 K when oxidation of the surface layers of Pd metal and CO oxidation by oxygen are very fast. Polycrystalline palladium foil with dimensions 10 × 5 × 0.04 mm was used in the study. The sample was treated in the feed containing 2 % CO, 10 % O_2 and 88 %He in a quartz flow reactor at ~1 atm pressure and 1.5 l/h flow rate at 800, 900 and 1000 K for 3 hours. The surface microstructure was studied using a scanning electron microscope SU8240 (Hitachi).

In the CO + O_2 reaction medium at T = 800-1000 K oxygen dissociatively chemisorbs on the palladium surface, penetrates into subsurface layers and dissolves in the metal. These processes result in the formation of a surface oxide film on palladium with the thickness ca. 2-3 nm where PdO particles with dimensions 5-10 nm are formed. These particles gradually produce a continuous oxide layer with the thickness 200-300 nm. CO molecules from the gas phase react with O atoms in the surface layer of PdO particles with desorption of gaseous CO_2. This reaction results in the formation of surface oxygen vacancies and adsorbed Pd_{ads} atoms. The Pd_{ads} atoms migrate on the oxide surface and form nuclei of metal particles, which rapidly grow due to fast generation of Pd_{ads} atoms in the CO oxidation reaction. Preferential formation of Pd_{ads} atoms at the grain boundaries of the oxide layer leads to the rupture of this layer along these boundaries with the formation of pyramidal fragments with the height 200-300 nm containing palladium metal particles at the top. At these conditions the pyramidal fragments of the oxide layer are gradually transformed into PdO crystals with the sizes about 200-300 nm. The CO reaction with oxygen atoms is different on the surface of PdO crystals than on PdO particles due to decelerated filling of surface vacancies by O and Pd atoms diffusing from the bulk to the surface. As a result, the concentration of oxygen vacancies and Pd_{ads} atoms on the surface of the oxide crystals increases. In addition, Pd_{ads} atoms are bound to the surface of PdO crystals much weaker than to the surface of PdO particles. Therefore, Pd_{ads} migrate faster on the surface of crystals forming metal particles and are also desorbed into the gas phase. Higher concentration of Pd atoms in the border gas layer initiates growth of particles and Pd crystals with low defect concentration. Pd crystals merge and gradually form aggregates and elongated structures producing a continuous surface layer.

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PP-100

Selective hydrogenation of citral to citronellal over nickel-chromium catalyst in the flow unit by continuous method

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A feature of the liquid-phase catalytic processes is the ability to produce complex compounds under relatively mild temperature conditions.

In industry citronellal prepared batch wise in an autoclave, a flow method for replacing this method will increase the productivity of the process.

It should be noted that in the literature as well as in industry of almost no data for the selective hydrogenation of organic substances on stationary catalysts in the liquid phase. Research in this area allow you to choose the optimal suspended and stationary catalysts and conditions for batch and continuous process for the hydrogenation of citral to citronellal.

When the hydrogenation of organic compounds take place in flow installation by method of "backflow" selection of catalyst particle size is of great importance. When the catalyst particle size is less than 1.5 x 2.0 mm, the substance does not pass through the catalyst bed is clogged in a reactor. With a larger catalyst particle size, hydrogenation of citralnot occurs completely. By varying the size of the catalyst particles and the rate of bubbling excess hydrogen can finely adjust the thickness of the liquid film covering the catalyst and its continuity.

We studied the effect of catalyst particle size (1.0 × 1.5 mm, 2 × 2.5 mm and 4 × 5 mm) from the bubbling speed of excess hydrogen (from 25 to 200 ml/min), at the test temperature 30 °C and the hydrogen pressure in the flow unit (from 5 to 100 atm).

Initial experiments on the hydrogenation of citralin the flow installation by method of "backflow" showed that the composition of catalyzate varies significantly depending on the defined concentration of hydrogenated substances. At chosen conditions hydrogenation of citralis non selective, citronellal formed along with citronellol and 3,4-dimetiloktanol. Thus, at a feed rate of citral ethanol solution of 0.6 mL/min with increasing concentrations of citral from 10 to 20 % yield of citronellal increases from 52 to 61 %, and the yield of citronellol from 7-9 % to 17-18 %.

Thus, the basic parameters of the hydrogenation of citral to citronellal in the flow unit over the nickel-chromium catalyst were found: at an experiment temperature of 30 °C, the amount of catalyst (2.5 mm x 2), hydrogen pressure (5-10 atm) and a rate of bubbling hydrogen (200 ml/min). Based on these data it is concluded on the need to modify the stationary nickel-chromium catalyst for increasing the selectivity of the process.

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Oxide $Ag_2Cu_2O_4$ as catalyst for CO oxidation at room temperature

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Mixed silver-copper oxides $Ag_2Cu_2O_3$ and $Ag_2Cu_2O_4$ are new interesting materials for catalytic applications owing to unique crystal and electronic structure [1,2]. Previously, we have performed the detailed study of low-temperature catalytic CO oxidation over oxide $Ag_2Cu_2O_3$ [3]. However, no any data about catalytic activity of $Ag_2Cu_2O_4$ can be found. This work is devoted to the catalytic study of oxide $Ag_2Cu_2O_4$ in comparison with $Ag_2Cu_2O_3$.

Oxides $Ag_2Cu_2O_3$ and $Ag_2Cu_2O_4$ were synthesized by co-precipitation in alkali solution using copper (II) and silver (I) nitrates. Catalytic activity was tested at 20°C in the reaction of CO oxidation using an automatic setup equipped with a plug flow reactor and a mass-spectrometer for gas analysis. As-prepared oxide $Ag_2Cu_2O_4$ with crednerite crystal structure was able to oxidize 100 ppm CO in an O_2 excess for 80 min, while only 70-80 % of CO conversion was reached in case of oxygen absence. It indicated the room temperature catalytic activity of $Ag_2Cu_2O_4$. After 80 min of complete oxidation over $Ag_2Cu_2O_4$ the CO conversion value was observed to be decreased up to 20 % during additional 100 min. Based on *in situ* XRD data no change of phase composition was observed during prolonged exposure by the reaction $CO + O_2$ mixture at room temperature. So, the deactivation of $Ag_2Cu_2O_4$ at room temperature was occurred as a result of surface modification only. Additionally, the activity of $Ag_2Cu_2O_4$ in CO oxidation was significantly dropped in the presence of water vapours in reaction mixture. It is noteworthy that oxide $Ag_2Cu_2O_3$ demonstrated no catalytic activity in CO oxidation at 20 °C, and heating up to 50-60 °C only resulted in the appearance of activity.

Also, TPD/TPR studies of $Ag_2Cu_2O_4$ were carried out using CO flow. The amount of CO consumed by $Ag_2Cu_2O_4$ was found to be noticeably more than quantity of emitted CO_2. It was concluded that hydroxyl species took a part in CO adsorption on $Ag_2Cu_2O_4$ surface. So, the formation of weakly bounded carbonates/hydrocarbonates can be considered as a reason for deactivation of $Ag_2Cu_2O_4$ during interaction with CO oxidation at room temperature.

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0003 for Boreskov Institute of Catalysis and was supported by RFBR grant No.16-33-00202.

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PP-102

Chaos in oscillatory recombination of hydrogen and oxygen on Pd-based catalysts

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The catalytic recombination of $2H_2 + O_2 \rightarrow 2H_2O$ is a key concept in the passive safety of nuclear reactors. To mitigate the hazard of gaseous H_2, the passive autocatalytic recombiners (PAR) are installed inside the nuclear reactor containment as safety devices [1]. The Pd/Al_2O_3 type catalysts are often used.

The reaction is highly exothermic. The Microscal gas flow-through microcalorimeter has been applied to monitor the heat evolution during the $H_2 + O_2$ recombination concurrently with the hydrogen consumption, using various hydrogen concentrations (6.2, 7.2, 8.6 % vol. H_2) in mixtures with synthetic air over Pd/Al_2O_3 catalysts at ambient conditions.

Kinetics of the catalytic recombination can reach oscillatory regimes. Two kinds of thermokinetic oscillatory dynamics: the quasiperiodic and the aperiodic oscillations both occurred spontaneously in the process, the latter confirmed to represent mathematical chaos [2]. The differential heats of process showed the thermal effects reaching as much as 700 kJ/mol H_2, thus exceeding the standard, thermodynamic heat of the H_2O formation from H_2 and O_2 (242 kJ/mol H_2) nearly by a factor of three.

The anomalous heat evolution is likely related to stepwise nature of the sorption and heat evolution in the Pd/H system [3]. Previously, the oscillations in the Pd/H_2 system, in oxygen-free environment have been explained in terms temporal separation of two steps, the first consisting merely of adsorption of H_2, and the second involving the dissociation of H_2 as well as the penetration of H species into the Pd bulk. The atomic hydrogen species may interact with molecular oxygen. The heat of H_2O formation from the atomic H and molecular O_2 should be around 680 kJ/mol H_2 that is very close to the actually observed values.

It is clear that the oscillatory kinetics as well as the anomalously high thermal effects both may pose a considerable engineering challenge in the PAR design proceedings.

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PP-103

Effect of the Si/Al ratio on the adsorption/desorption properties of zeolites towards toluene

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Nowadays, a problem of exhaust gases purification is of great importance. Despite a number of the catalysts developed to neutralize outgoing gases of gasoline and diesel engines, their effective use requires compliance with temperature regime. The catalyst should be heated over light-off temperature. During the engine start, few minutes pass before the temperature reaches ignition value, while the pollutants come to the atmosphere untreated.

Few approaches were proposed to solve the “cold start” problem. The first one considers the use of additional adsorber, which traps and stores unburnt hydrocarbons, located before the three-way catalyst brick. Rise of the exhaust gases temperature up to 200 °C causes desorption and subsequent conversion of the hydrocarbons on the catalyst. Currently, research works performed in this direction are aimed with a search of appropriate composition of adsorptive materials. It is known that zeolites, especially doped with Ag, are characterized with high adsorption ability towards aromatic hydrocarbons – the most toxic components of fuels. Since the water vapors are present in exhaust gases, the properties of adsorbents depend on module of used zeolite. The hydrophobicity of zeolite increases along with Si/Al ratio rise that should facilitate the competitive adsorption of hydrocarbons.

From the other side, competitive adsorption of toluene and water is known to be affected by the adsorptive sites based on Ag species located on 5T clusters of zeolite. It testifies towards the possibility of efficient application of low-modulus (hydrophilic) zeolites, which are more advantageous in terms of hydrothermal stability.

The purpose of present work was to reveal the effect of zeolite Si/Al ratio on toluene adsorption at 100 °C with variation of silver loading. Two desorption regions were studied: 100-200 °C (weak adsorption) and 200-400 °C (strong adsorption).

As it was found for ZSM-5, amount of strongly bonded toluene increases with a growth of Ag loading and goes through the maximum, while the weakly bonded toluene capacity decreases. In the case of β-zeolite, total toluene capacity reaches the maximal value at silver loading of 6-7 %. No difference was found for the samples with modules of 25 and 30. Linear dependence of amount of the strongly bonded toluene on Ag loading was observed for Y-zeolite, including final investigated point of 8.8 wt. % Ag. This sample, having the lowest Si/Al ratio, showed the maximal value of strongly bonded toluene adsorption. In contrary, sample based on ZSM-12 exhibits the worst adsorption/desorption properties, which can be attributed to the highest zeolite module and hydrophobicity.

PP-104

Water as an activator for the nickel-containing Ziegler-type catalysts of an ethylene oligomerization

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The catalytic activity of Ziegler systems in the reactions of lower alkenes oligomerization determines by several factors. In spite of a long period of research and industrial use of the nickel Ziegler systems the question about the role of water (and other proton-donor compounds) in the formation and functioning of concerned catalytic systems are still open to debate.

The report focuses on the study of the H_2O influence on the formation and functioning of the ethylene oligomerization catalysts. Systems based on the $Ni(acac)_2$ and chloro organo-aluminium compounds ($AlEt_2Cl$, $Et_2AlCl{\cdot}Cl_2AlEt$) were selected as the model systems.

It is found that TON and TOF values of the considered systems are quite low by using virtually "dry" starting components, including solvent – toluene. For example, TON = 790 (mol C_2H_4)/(mol Ni) and average value of TOF = 45 min^{-1} for an ethylene oligomerization by $Ni(acac)_2$–$50AlEt_2Cl$ system in toluene ($C_{Ni\ subl.} = 2.5{\cdot}10^{-3}$ mol/l, T=286 K, $C_{H2O} = 1.71{\cdot}10^{-3}$ mol/l). It is shown that TON and TOF of the catalyst systems depends not only on the nature of cocatalyst, Al/Ni ratio, the concentration of the starting components, but also on the C_{H2O} in the solvent. The latter dependence has extreme character. TON and TOF values of the considered catalytic systems increased by 9-10 times at optimum C_{H2O}, compared with the values of TOF and TON for the «dry» systems. Increase of the C_{H2O} in toluene have an effect on the quantitative composition of the products, namely, increasing the proportion of methylpentenes and linear hexenes, but fraction of butene-2 decreased, with the proportion of butene-1 does not change. In addition, the small amounts of toluene alkylation products was find in the catalyzate solution, it proportion increases with increasing of C_{H2O} in toluene.

Analysis of the obtained results allows formulating the conclusion that the water plays an important role in the formation and functionalization of the catalytically active in the ethylene oligomerization and the alkylation of aromatic hydrocarbons systems of the Ziegler type. A scheme of the mechanism of an ethylene oligomerization catalysts formation, which includes the step of reacting an Brønsted acid ($AlR_xCl_{3-x}{\cdot}H_2O$) with Ni(0) complexes is proposed.

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PP-105

The role of proton-donor compounds in the formation of hydrogenation Ziegler catalysts

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Previously it has been shown that the activity, productivity and selectivity of Ziegler type catalyst systems depends on several factors, for example, the nature and concentration of the precursors, temperature and nature of solvent. In our earlier studies both positive and negative influence of water present in the composition of the precursors, or added to the system, on the quantitative parameters (turnover frequency (TOF) and turnover number (TON)) of investigated catalysts was founded [1-3].

The report presents the results of studies of the proton-donor compounds action (H_2O, alcohols, acids) on the quantitative characteristics of the catalytic systems based on bis(acetylacetonate) palladium, cobalt, nickel and $AlEt_3$, $Al(OEt)Et_2$, $LiAlH_4$ or $NaBH_4$. It was found that by using a well "drained" solvents ($C_{H2O} = 1.0\text{-}2.0 \cdot 10^{-3}$ mol/l) inactive or low active in the styrene hydrogenation systems are formed. The addition of proton-donor substances causes a sharp increase in the TOF and TON of formed catalysts. It has been shown that not only the quantity but also the nature of proton-donor compound determines the promotional effect.

Moreover, by the TEM method on the example of nickel and cobalt catalysts it has been shown that homogeneous, inactive in catalysis systems are formed in the absence of H_2O. The nanoscale metal particles formation and the increases of the hydrogenation activity were observed when H_2O (or alcohol) was added to the catalyst solution. Based on data of the kinetic experiments, and the results that was obtained by multinuclear NMR spectroscopy, ESR, UV-, and IR- spectroscopy the model of the nanoparticle ligand shell was specified. It can explain the activating effect of the proton-donor compounds on the formation of hydrogenation catalysts [2].

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PP-106

Kinetic study of low-temperature catalytic steam reforming of light hydrocarbons over the Ni-based catalyst

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In recent years, associated petroleum gas (APG) utilization approaches are focused mainly on the generation of electric power, which can be used for both local needs and transported for long distances. Direct use of APG as fuel for power generation is limited by low methane content, unstable gas composition, high coking and detonation risks that decreases service life and causes engine damage. Low-temperature catalytic steam reforming of light hydrocarbons (LTSR) represents a promising way to convert APG into methane-enriched gas fuel that can be used for electric power generation.

LTSR occurs at T = 200-350 °C and atmospheric pressure over Ni-based catalysts. The process kinetics could be described by two brutto-reactions:

1) $C_nH_{2n+2} + 2nH_2O \rightarrow (3n+1)H_2 + nCO_2$ (n = 3, 4, 5 in our study)

2) $CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$

In our work we have shown that reaction (2) is quasi-equilibrium at T > 250 °C and thus the total rate of the LTSR process is limited by the reaction (1). Effective reaction orders with respect to C_3H_8, C_4H_{10}, and C_5H_{12} are close to one; reaction order with respect to steam is slightly negative or close to zero. Variation of CH_4, CO_2 and H_2 concentrations does not significantly affect on the hydrocarbons conversion. Effective activation energies of C_3H_8, C_4H_{10}, and C_5H_{12} steam reforming are close to each other and range from 120 to 150 kJ/mol. Ni-based catalysts are not affected by carbon deposition under reaction conditions due to kinetic inhibition despite this side process is thermodynamically possible.

Based on the two-stage macrokinetic model the mathematical simulation of LTSR of model CH_4-C_5H_{12} mixtures was performed. Comparison of the simulated and experimental data (Fig.1) shows that proposed model describes well the observed dependences and so, can be used for catalytic reactor design.

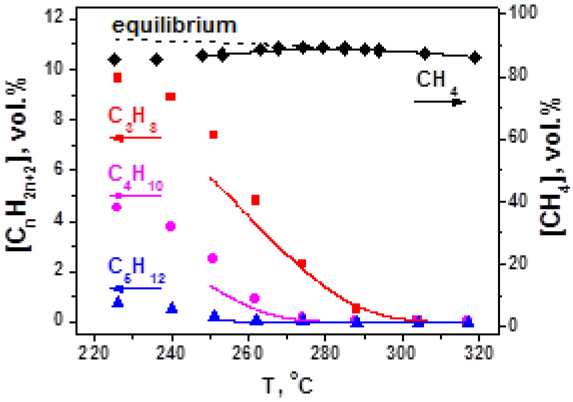

Fig. 1. The temperature dependencies of CH_4, C_3H_8, C_4H_{10} and C_5H_{12} concentrations (on dry basis) in the LTSR of model mixture. Points - experiment, lines - modelling. $H_2O/C = 0.5$.

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Weakly bound oxygen in the Mn-Ga-O spinels: features of oxide reduction and catalytic activity

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The interest in mixed manganese-containing double oxides with the spinel structure is caused by their wide application in various industries. High mobility of oxygen makes it possible to employ the manganese-containing oxide systems as catalysts in oxidative processes of methane dimerization, deep oxidation of hydrocarbons and CO and syngas production from associated petroleum gases. At the present time, Mn-Al oxide systems are well studied, such systems are industrial catalysts of deep oxidation of hydrocarbons to CO_2 and H_2O. Gallium is considered as a chemical analog of aluminum, but Mn-Ga-O spinels have not been investigated earlier, therefore, it is interesting to study their oxidation-reduction properties.

A series of manganese-gallium oxide samples obtained by coprecipitation, followed by calcination in argon in a wide temperature range of 600-1200 °C was investigated. The presence of weakly bound oxygen in the samples obtained at 600-800 °C was shown by the TGA and TPR methods. According to TGA, there is a weight loss (3.4-0.5 %) when heated in inert atmosphere. According to TPR, there are low-temperature hydrogen absorption peaks located at 500 °C. The presence of "excess" oxygen in the spinel structure, in which a cubic close packing of oxygen is realized by forming cation vacancies in the octahedral and tetrahedral sites. The excess negative charge in comparison with the "ideal" spinel is compensated by increasing the content of Mn^{3+} in the oxide composition. This is confirmed for manganese cations on the surface by XPS.

Hydrogen reduction process of Mn-Ga-oxide was investigated. Two-stage reduction of samples obtained at 600-800 °C was observed. At the first stage, the leaving of the "excess" oxygen takes place, as evidenced by the results of TPR and in situ XRD. The increase in the lattice parameter correlates with the change in the surface composition fixed by XPS. It indicates that the change in the volume of oxide leads to change of the sample surface. During reduction, the leaving of "excess" oxygen is accompanied by enrichment of the surface by the manganese cations. At the second stage, there is a transformation of Mn^{3+} to Mn^{2+} cations in the spinel structure with segregation to the MnO phase. A correlation between the content of weakly oxygen in the Mn-Ga oxides and their catalytic activity in the oxidation of CO was detected.

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PP-108

Formation of O^- radical anions in oxide materials and their reactions

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O^- radical anions are the most reactive oxygen intermediates in catalytic and photocatalytic oxidation reactions taking place on oxide catalysts. Sometimes they can be stabilized on the surface or in the bulk of oxides and be detected by EPR spectroscopy. Here we shall present the data on the formation mechanisms of such radical anions and reactions with their participation obtained at Boreskov Institute of Catalysis SB RAS using “in situ” EPR spectroscopy. The following main types of reactions with significantly different formation mechanisms of O^- radical anions will be discussed:

1. Photostimulated processes in the surface absorption band of the oxides (MgO, CaO, TiO_2, ZnO, etc.) leading to the formation of O^- radical anions by homolytic dissociation of surface hydroxyl groups [1].

2. Reoxidation of V/SiO_2 catalysts accompanied by the formation of O^- and O_2^- radical anions [2].

3. Formation of α-oxygen ($[Fe^{3+}\text{-}O^-]$ complex) in Fe-ZSM-5 zeolites, methods of its detection using EPR spectroscopy and comparison of its reaction with those of “conventional” observable O^- radical anions in oxides [2].

4. Appearance of bulk O^- radical anions in calcium-aluminate materials with C12A7 structure, unusual mechanism of their formation ($O^{2-} + O_2 \Leftrightarrow O^- + O_2^-$) and possible participation in catalytic oxidation reactions on such materials.

In addition, the structure of different types of O^- radical anions on the MgO surface and some reactions with their participation were studied by quantum chemistry methods [1, 3].

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Photocatalytic activity of ZnS nanoparticles with random close-packed structure

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The intense search for renewable and economically liable sources of energy has spurred much interest in semiconductor-based devices capable to convert solar energy into electricity. ZnS is abundant, chemically stable, nontoxic material that is appropriate for building such devices. The wide band gap of wurtzite-type ZnS (3.91 eV) is well suited for absorption in the ultraviolet region of the electromagnetic spectrum, but is too large for absorption of visible light [1]. Our recent work demonstrated that chemical bath deposition (CBD) could produce nanocrystalline ZnS powders with a crystal structure differing from the wurtzite *B*4 (hcp) and sphalerite *B*3 (fcc) lattices typical of this material, which is identified as random close packing (rcp) [2]. Using rcp-ZnS nanoparticles, nanocrystalline ZnS can be used in photocatalytic processes.

In this study, we investigate photo-degradation of hydroquinone $C_6H_4(OH)_2$ (HQ) under blue light irradiation using rcp-ZnS (Fig.). The major theme is to assess the future feasibility of rcp-ZnS for large-scale photo-degradation processes, in terms of efficiency, recovery and environmental friendliness. Photo-degradation of HQ using wide band gap semiconductor ZnS has not been reported earlier.

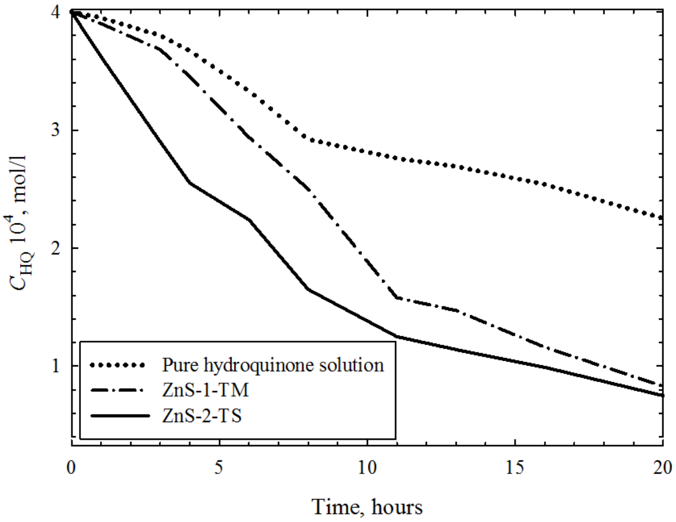

Fig. The kinetics of catalytic oxidation of HQ aqueous solutions under visible light irradiation (440-460 nm) without and in presence of rcp-ZnS prepared by CBD using thiourea (ZnS-1-TM) and disodium thiosulfate (ZnS-2-TS) as sulfur sources

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Features of Formation and Mechanism of Propane Conversion over the Active Sites of Elementoaluminosilicate Catalysts

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The priority direction of basic research in the field of catalysis is the study of the mechanism of catalytic reactions at the atomic and molecular level. The main objective in this case is to understand the nature of the states of active sites through which their structure forms and transforms. The purpose of this paper is to establish the effect of the nature of the active centres in modified zeolite catalysts on their reactivity in the course of propane conversion into aromatic hydrocarbons. The elementoalumosilicates (E-AS) with the structure of ZSM-5 zeolite containing Zn, Zr, and In were the objects of investigation.

The catalytic studies have shown that zeolites with additions of modifying elements exhibit relatively high reactivity in the process of propane aromatization, the zeolite catalyst system with addition of zinc being the most selective and active. A more than 0.81 % increase in the concentration of zinc oxide contained in the catalyst results in a slight decrease in conversion and increase in its aromatization activity. In the presence of Zr-AC sample as in the case of Zn-aluminosilicate a noticeable formation of aromatic hydrocarbons from propane is observed at temperature 550 °C and above. However, unlike the Zn-containing zeolite the increase in concentration of zirconium in a catalyst results in a decrease not only of total activity but also of aromatization activity, so the selectivity towards formation of aromatic hydrocarbons over the 3.64 % Zr-AC sample at 600 °C is 7.2 % for a propane conversion 54 %. The reaction products formed over this catalyst contain a large amount of lower C_2-C_4 olefins. Of all catalysts under study, the In-AC sample exhibits the lowest activity the catalysts under study during propane conversion.

Using data of structural and morphological studies of elementoalumosilicates it was found out that the introduction of Zn, Zr, and In into a zeolite results in a partial morphological change.

Investigation of the electronic state of active sites has shown that In and Zn cations are fixed to oxygen ions in the channels of zeolite, In being partially localized on the outer zeolite surface. The high value of the Zn3d binding energy explains the low mobility of zinc in a catalyst during the heating with a beam of electron microscope. Relatively low Zr3d and In3d binding energies cause clustering of zirconium and indium ions when heated by an electron beam, which occurs simultaneously with the destruction of zeolite channels.

The analysis of the data obtained indicates that the introduction of various modifying additives into a zeolite at the step of hydrothermal synthesis results in a yield of catalysts with different functional properties.

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PP-111

Deactivation of Pt-Rh catalysts of ammonia oxidation

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A process of ammonia oxidation on Pt-Rh catalysts is rather well investigated and introduced into operation as industrial nitric acid units in Russia (Ukl-7, AK-72). The reaction rate under oxidation conditions (t = 850 °C and P = 0.45-0.72 MPa) is very high (contact time is (1-2)*10^{-4} sec) and the reaction proceed in the field of external diffusion. The catalyst is used as metallic woven and knitted messes. The industrial reactor using diameter 1.7-1.9 m include a packet of 10-12 Pt-Rh nets, each net being about 2 kg. There are 23-25 kg of catalyst in the packet.

During the operation the catalyst under process conditions (T, P, linear stream velocity) decays and the stream seizes small particles of the catalyst. During a period of 3000-5000 hours the mass of nets loses 30-50 %. As it follows from paper [1] under process conditions (850-900 °C) the surface of the catalyst loses not Pt atoms, but oxide PtO_2: reaction $Pt_s + O_2 = PtO_{2\,gas}$ and then was shown the rate of oxidation is a function not only of the temperature of the platinum, but also of the temperature and pressure of the gas. Taking into account that the catalyst surface is almost completely covered by oxygen and a fraction of surface occupied by other components can be neglected, we can write the rate of catalyst "chemical evaporation" and respectively, it's mass diminishing as follows:

$$r = A\frac{P_{O_2}}{1 + K_1 P_{O_2}} \qquad (1)$$

here $A = A_0 e^{-\frac{E}{RT_S}} * P_e * \frac{1}{\sqrt{T_g}}$,

r – the rate of "chemical evaporation" of Platinum, г$_{cat.}$/(m^{2}day); P_{O_2} – oxygen partial pressure, atm; T_g – gas temperature, ^{0}K; K_1 – adsorbtion factor, atm^{-1}; $A_0.P_e$ – experimental factor, g$_{cat.}$(^{0}K)$^{0.5}$/(m^{2}day.atm); E = 42500 cal/mol; R = 1.987cal/mol/^{0}K.

The structure of "evaporation" rate (1) was used in mathematical simulation of transient process of ammonia oxidation on Pt-Rh catalyst.

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PP-112

EXAFS study Pt, PtMe supported catalytic nanosystems

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In recent years, few new types of carbon supported catalysts, such as activated carbon fibers, Busofit and CNF carbon nanofibers-based catalysts, inspire a growing interest. As rule, Busofit and CNF based catalysts have improved catalytic selectivity, activity and thermostability as compared to the traditional carbon supported catalysts using carbon-black or Sibunit as supports. This modification of catalytic properties is believed to result from higher accessibility of the deposited active component to the reactants and from strong interactions between the catalyst particles and the support surface. This work is devoted to the comparative structural study of few promising Pt, Pt-Me carbon-based catalytic systems using different carbon supports by the EXAFS methods: 1) Pt, Pt-Me Busofit-based catalysts for CO oxidation; 2) Pt, Pt-Me CNF-based cathode catalysts for PEMFC; 3) Pt, Pt-Me Sibunit-based catalysts for hydrocarbon conversion. Mesoporous granular carbon composite – Sibunit and carbon active fibers Busofit (as woven activated carbon fabric modified with thermally stable acid groups) was used for prepaation of supported metal catalysts. Platinum in Pt- and PtMe-forms of Busofit was introduced from $Pt(NH_3)_4Cl_2$ aqueous solution by means of impregnation and ion-exchange. A series of CNF with different arrangement of graphitic planes were synthesized by decomposition of methane and ethylene over transition metal catalysts. These structural types of CNF were used for preparation of the Pt, Pt-Me catalysts for PEMFC cathodes. Various synthetic techniques were studied, using H_2PtCl_6 and other Pt complexes as Pt precursors. All EXAFS spectra of the studied samples were recorded at Siberian Synchrotron and Terahertz Radiation Center (SSTRC, Novosibirsk). The local Pt and Me (Fe, Cu, Co) arrangements of all the samples studied were established and the phase compositions were determined. It was shown that there are some differences of the metal arrangements for the studied systems. All possible structural models were discussed. In addition, these samples were studied by the TEM, EDX and X-ray diffraction methods. The data of all methods are in a good agreement.

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XAFS study of catalytic nanosized systems promising for alternative energy and environmental catalysis

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Recently, low-content supported mono- and bimetallic catalytic nanosystems, containing transient and noble metals cause great interest to researchers, because of their practical application for a wide range processes promising for alternative energy and environmental catalysis; owing to the possibility of varying catalytic properties, relatively low cost of the final products, ease of recovery of expensive components of the exhaust catalysts.

The samples of modeled catalysts ~0.1-1 % Me_1Me_2 (Me_1= Au, Pt, Pd, Ru and others) were obtained by varying preparation methods of active component formation (*deposition-precipitation*, zol-gel, *ion exchange*, *MOCVD*) from mono- and hetero-metallic precursors of different nature. Nanoparticles of active component were located on various supports (C, SiO_2, Al_2O_3, TiO_2, ZrO_2) and different activation and reduction conditions were used. All XAFS spectra of the studied samples were recorded at SSTRC, Novosibirsk. The study of the genesis of the active component of the local structure, including the study of initial precursors and catalysts after reduction and change the state of the active component were carried out. It was shown that, depending on the prehistory, the formation of different (metals, metal-oxides, oxides) nanosize forms of precious metals, which are located on the surface of the supports. Genesis of the state and local structure arrangement of supported metal nanoparticles of the studied catalytic nanosystems was characterized in detail. Correlations between their catalytic properties, local structure distortions and state of metal components were demonstrated. It was shown that, depending on the prehistory, the formation of different (metals, metal-oxides, oxides) nanosize forms of precious metals, which are located on the surface of the supports. The interatomic distances and corresponded coordination numbers were calculated by fitting. All possible structural models were discussed. *Additionally, morphology and composition of the samples of catalysts were studied by the* TEM, XRD, XPS methods.

Acknowledgement. The work was done using the infrastructure of the Shared-Use Center “Siberian Synchrotron and Terahertz Radiation Center (SSTRC)” based on VEPP-3 of BINP SB RAS. This work was supported by RFBR (163350249, 163350248, 160301139, 163350250), SB RAS comprehensive program II.2P (Project 0305-2015-0018).

PP-114

Diffraction effects of nanosized particles

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Nanocrystalline materials are of considerable interest because particle morphology to affect physicochemical properties. Investigation of the relationship between properties, atomic structure and nanostructure of materials is an actual problem. This can appear as anisotropic broadening of the diffraction peaks, redistribution of the intensities or appearance of diffuse scattering.

The method based on the Debye scattering equation [1] is known in the literature as Debye Function Analysis (DFA) [2]. It is full-profile method which is applicable for any an arbitrary atoms collection, and therefore can be used for crystalline objects, non-crystalline materials or nano-structured objects. For this purposes the approaches are developed based on previously submitted program [3]. It is public-domain software and available on the website: www.sourceforge.net/projects/dianna.

Possibilities of modelling diffraction patterns by DFA method for solution and refinement of the atomic structure, determination of the shape and sizes of nanoparticles will be showed for specific examples of various nanocrystalline materials.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00037.

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PP-115

The composition of the adsorbed layer of variously prepared titanium dioxide under ambient air

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Storage powdered titanium dioxide in air results in the formation on its surface adsorbed layer whose composition is determined by the composition of the gas phase of air and surface adsorption capacity of titanium dioxide particles to these gases. After contact with the air before to the experiments with TiO_2 often carry out additional high-temperature treatment, which changes not only the adsorbed layer, but the surface layer of the titanium dioxide lattice. This kind of treatment can completely remove the adsorbed layer of TiO_2. This condition is not typical for TiO_2 surface during the catalytic and photocatalytic processes in the gas phase at room temperature and, moreover, in a liquid medium. If cleaning of the surface after contact with the atmosphere not to carry out, the state of the adsorbed layer can significantly affect the obtained experimental results. As a result of this, it becomes necessary to monitor the state of the adsorbed layer, especially in cases when the specific surface of the powder sample is large (tens to hundreds $m^2 \cdot g^{-1}$).

To determine the composition of TiO_2 adsorbed layer after contact with the ambient air, in this work we investigated the following samples:

a). the powder-like titanium dioxide produced by grinding a titanium dioxide crystal under ambient air. The powder specific surface was equal to 1.6 $m^2 \cdot g^{-1}$;

b). the powdery titanium dioxide prepared by combustion pyrotechnic mixture consisting of ammonium perchlorate, hydroxyl-terminated polybutadiene and titanium particles (particle size from 60 to 90 μm) under ambient air. The highly dispersed titanium dioxide powder had the specific surface area of 6 $m^2 \cdot g^{-1}$;

c). the plasmatronic nonporous TiO_2 (“Degussa”) with a surface area of 48 $m^2 \cdot g^{-1}$.

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PP-116

Low-spin and high-spin oxoiron(V) intermediates that oxygenate strong C-H bonds

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The regio- and stereospecific oxidation of aliphatic C-H groups of organic molecules is a very challenging problem, attracting great attention of catalytic chemists. The significant progress in the search of the synthetic systems capable of oxidizing aliphatic C-H bonds with preparatively acceptable activity and selectivity is associated with the use of complex **1** (Figure 1) in combination with H_2O_2 as oxidant, and acetic acid as additive.

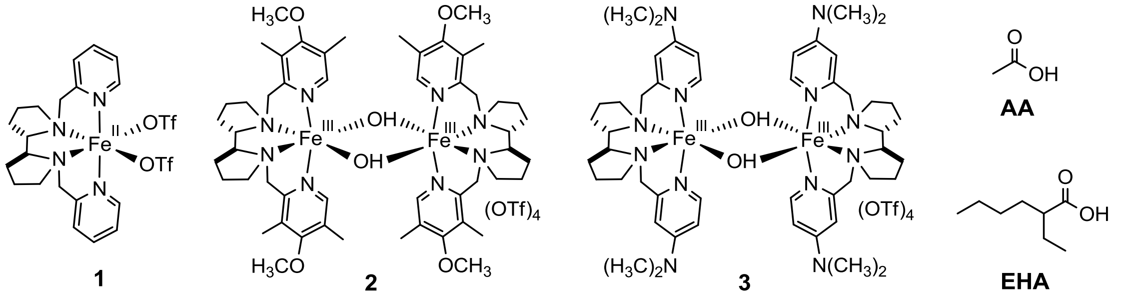

Figure 1. Structures of complexes

It is generally accepted that the oxoiron(V) intermediates are active oxidizing species of this type catalyst systems. We have found that the low-spin (S =1/2) (g_1 = 2.07, g_2 = 2.01, g_3 = 1.96) and high-spin (S =3/2) (g_1, g_2 = 3.96, g_3 = 1.95) oxoiron(V) intermediates (**2a** and **3a**) are formed in the catalyst systems **2**/H_2O_2/RCOOH and **3**/H_2O_2/RCOOH, respectively (RCOOH = acetic acid or 2-ethylhexanoic acid) (Figure 2). It has been shown that **2a** is kinetically competent for breaking strong C-H bond of cyclohexane (BDE ~ 100 kcal·mol^{-1}). The catalyst systems **2**/H_2O_2/RCOOH and **3**/H_2O_2/RCOOH, exhibiting the low-spin and high-spin oxoiron(V) intermediates have been compared in the chemoselective oxidation of cyclohexane and regioselective oxidation of adamantane. It was found that catalyst systems exhibiting the high-spin oxoiron(V) intermediates are more chemo-and regioselective in C-H hydroxylation, than those displaying the low-spin congeners.

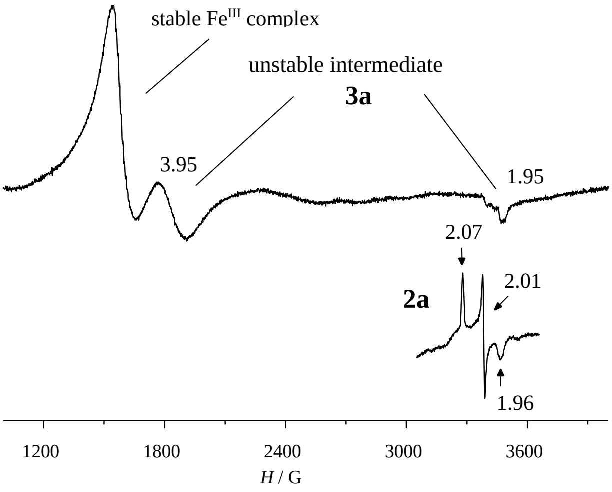

Figure 2. EPR spectra of **2a** and **3a**

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PP-117

Hydroamination of styrene by anilines using $[Pd(acac)(PR_3)_2]BF_4$-based catalyst system: precatalyst activation mechanism

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Transition-metal-catalyzed hydroamination of olefins is an efficient route to alkyl- and benzylamines from readily available reagents. One promising approach [1] is the addition of anilines to vinylarenes catalyzed by a combination of $Pd(OCOCF_3)_2$, phosphine and an acid with weakly coordinating anion such as TfO^-. Recently, our group showed that acetylacetonate-based cationic actylacetonate palladium complexes can be used as efficient precursors for the selective dimerization of styrene and telomerization of 1,3-dienes with diethylamine. In this report we present our recent study on the acetylacetonate cationic palladium complexes catalyzed intermolecular hydroamination of styrenes with anilines. Based on the results of Hartwig et al.[1], we investigated the hydroamination reaction using complexes $[Pd(acac)(PR_3)_2]BF_4$ and $[H\cdot OEt_2][BF_4]$ co-catalyst by employing similar reaction conditions. The reaction of aniline with styrene occurred to give the Markovnikov addition product in high selectivity after 20 h at 100 °C. When $BF_3\cdot OEt_2/i\text{-}PrOH$ mixture was applied as co-catalyst in the reaction TON was substantially increased. Compared to known catalysts $\{[Pd(acac)(PPh_3)_2][BF_4](\mathbf{1})/BF_3\cdot OEt_2/i\text{-}PrOH\}$ catalyst system showed higher activity and productivity. Previously reported mechanistic and DFT studies indicated that these type of hydroamination reactions involves an insertion of the styrene double bond into a Pd−H species [2]. In order to establish the catalyst activation mechanisms catalyzed by Pd(II) used in the experiments we analyzed the IR and NMR spectra of the reaction mixture $\mathbf{1}/S/nBF_3\cdot OEt_2$ (S = hexene-1, MeCN). E.g. in the case of reaction between **1**, $2BF_3OEt_2$, and $5CH_3CN$ in the ^1H NMR spectrum complicated resonances appeared (1.96 and 2.35 CH_3-acac, 1.96 CH_3-MeCN 4.19 CH-acac) from C-bonded acac group and coordinated acetonitrile. It is concluded that starting with BF_3-adduct, the first step of the catalytic reaction involves transformation of κ^2-O,O-acetylacetonate to η^3-oxoallyl intermediate, which leads to the formation of olefin's π-complex with γ-bonded acetylacetonate ligand. In the next steps, insertion of the coordinated styrene into the Pd–C bond and an external nucleophilic attack of the aniline to a η^3-benzyl complex occurred followed by formation of Pd(0)-bis-phosphine complex, which needs to be protonated [2]. One can assume that in our case $BF_3\cdot OEt_2/i\text{-}PrOH$ mixture gives Brønsted acid to continue the cycle. However, influence of the Brønsted acidity and precursors ligand structure on the catalyst selectivity still needs to be studied.

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PP-118

Probabilistic reliability prediction of chemical reactors for heterogeneous catalytic processes

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Has been proposed a mathematical model of the probabilistic prediction of reliability of reactors for heterogeneous catalytic reactions on the basis of a two-parameter family of absolutely continuous distributions, which are based on the law of distribution of Weibull-Gnedenko [1]. One of them is a two-parameter distribution probability density in modification:

$$f(t) = \frac{a}{T_{average}^{a}} t^{a-1} exp\left(-\left[\frac{t}{T_{average}}\right]^{a}\right), \tag{1}$$

where: a – is the parameter that changes when you switch to another condition of the reactor and/or process (and always $a \leq 3{,}5$); t – time trouble-free operation of the reactor; $T_{average}$– mathematical expectation of reactor trouble-free operation; parameter $a = \frac{dS(t)_V}{dt}\boldsymbol{Y}^i$, where: $\frac{dS(t)_V}{dt}$ – speed of aging (wear) of the body of catalyst in the volume V for a period of t, $\boldsymbol{Y}^i = \left[\, y_1^i \ldots y_K^i\right]^{\boldsymbol{T}}$ – the vector of observed parameters heterogeneous catalyzed chemical reaction in time t_i. Distribution function of the probability of failure (accident) of a reactor:

$$F(t) = 1 - exp\left(-\left[\frac{t}{T_{average}}\right]^{\frac{dS(t)_V}{dt}\boldsymbol{Y}^i}\right), \tag{2}$$

and the failure rate of the reactor: $\lambda(t) = \frac{\frac{dS(t)_V}{dt}\boldsymbol{Y}^i}{T_{average}}\left(\frac{t}{T_{average}}\right)^{\frac{dS(t)_V}{dt}\boldsymbol{Y}^i-1}$, (3)

and the mathematical expectation of trouble-free operation of the reactor:

$$T_{average} = \frac{G\left(\frac{1}{\frac{dS(t)_V}{dt}\boldsymbol{Y}^i}+1\right)}{\lambda^{\left(\frac{dS(t)_V}{dt}\boldsymbol{Y}^i\right)^{-1}}}, \tag{4}$$

where G(x) – is γ-function. It is possible to estimate the γ-interest period of the expectation of failure or accident of the reactor (0<γ<100):

$$t_\gamma = \frac{G\left(\frac{1}{\frac{dS(t)_V}{dt}\boldsymbol{Y}^i}+1\right)}{\lambda^{\left(\frac{dS(t)_V}{dt}\boldsymbol{Y}^i\right)^{-1}}} \sqrt[\frac{dS(t)_V}{dt}\boldsymbol{Y}^i]{-ln\left(\frac{\gamma}{100}\right)}. \tag{5}$$

The proposed mathematical model (1) – (5) can be useful for the development and operation of information management systems reliability and risk management of chemical-technological systems of new generation for multicomponent heterogeneous catalytic processes in the chemical industry.

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PP-119

Chemical grafting of platinum clusters for catalytic hydrogenation: structural and size effects on adsorption layer

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Nanoparticles (NPs) are a state of the matter far from thermodynamic equilibrium and, thus, the (nano)catalyst operating mode is essentially dynamic. The manipulation with surface energy of a given facet by using surface-binding molecules is the physico-chemical ground for major synthetic strategies of NPs. Moreover, self-assembled (sub)monolayers are found to be important for different applications, e.g., for catalysis where it can increase durability of NPs commonly exhibiting strong tendency to recrystallization and/or coagulation or even be a key factor for emergence of a modified active (stationary) state. However, data on specific adsorption energy are very scarce. In the present report, we addressed to these properties, namely, dissociative and non-dissociative adsorption of capping ligands on PtNPs surface for selective hydrogenation. The structural of energetic and structural data of the provided trial set are of importance for force-field attenuation in atomic scale modeling and computer-aided material design.

Quantum chemical study of (finite, free) clusters Pt_{25}\{100\} and Pt_{30}\{111\} (two-layer clusters), Pt_{41}\{100\} and Pt_{40}\{111\} (three-layer clusters) as models for different facets of Pt NPs corresponding to crystallographic planes was conducted at the BLYP/CRENBS(Pt)/Lanl2DZdp(S)/6-31G(d,p)(C,H) theory level. BuSH was used as a model for 1-dodecanethiol (DDT) commonly used as a surfactant. Different number of H_2 molecules was used to model a co-adsorbate. Multiplicities studied are 1, 3, 5, 7, 9, 11, and 13. On the basis of the presented computational results, it is possible to evaluate the reconstruction of the NP surface and metal–thiolate complex formation. The strong RS–Me bond provides an efficient anchor of the molecules to the metal substrates. No out of surface movement of Pt atoms were determined; however, in plane the reorganization is remarkable (0.2-0.3 Å). In conclusion, if there is no evidence of Pt out of plane surface reconstruction upon thiol adsorption, thus simple adsorbent models could be valid to describe this system. Works dealing with this model the thiolate–metal interaction simply as adsorbates on an unreconstructed metal surface are valid with respect to newer results. To our knowledge, there are no experimental data for thiol adsorption on the (100) and (111) platinum surfaces that we have explored here.

The exothermicity of the dissociative adsorption is reduced for the successive coordination of the BuS-group (averaged reaction energy is -112.8 kJ/mol). The adsorption energy is nearly independent on size of the cluster for the studied clusters if the same coordination mode is considered.

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PP-120

Reactions and dynamics of hydrogen on chemically modified Pt nanoparticles of various sizes. DFT and MD/ReaxFF study

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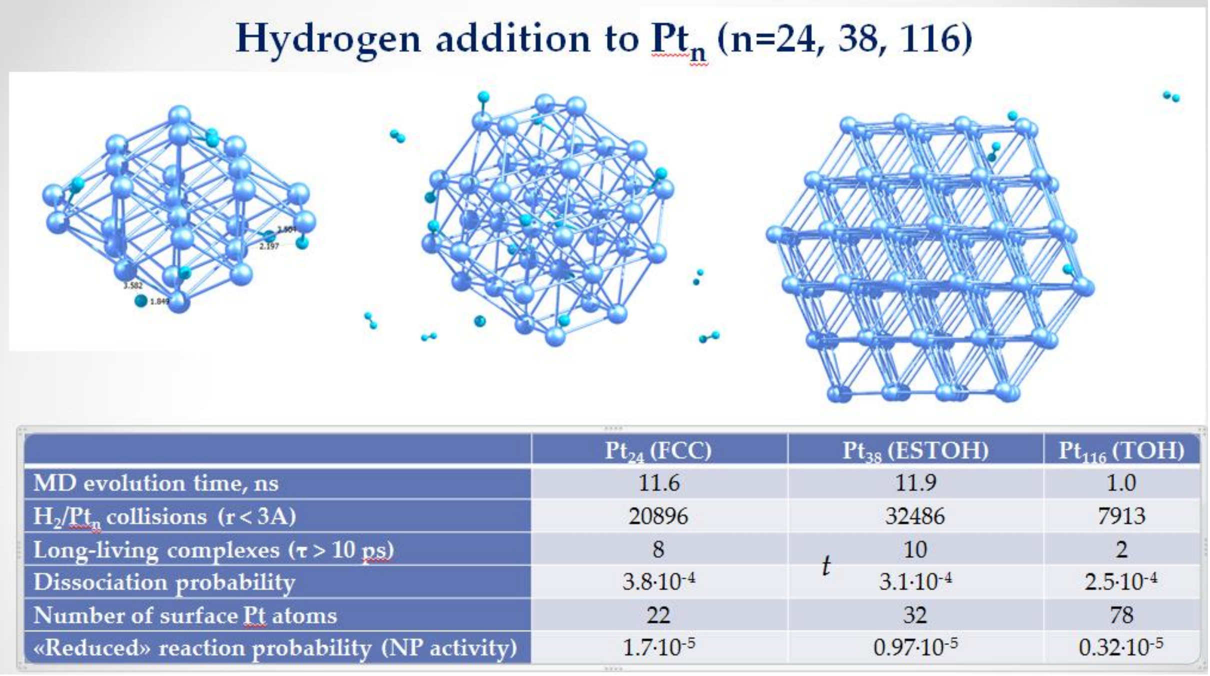
Platinum nanoparticles (PtNP) are prospective catalysts for highly regioselective and, probably, stereoselective hydrogenation of bifunctional organic species. In the present work, the hydrogen adsorption, dissociation and dynamics of hydrogen on the surface of chemically modified PtNPs were considered as initial steps of the unsaturated aldehyde hydrogenation resulting to unsaturated alcohols.

PtNP of various sizes were modelled by the Pt_n clusters with n = 13, 24, 38, 55, 116, 146, 201. For smaller representatives (Pt_{13}, Pt_{24}, Pt_{38}), the DFT calculations (BLYP/CRENBS(Pt,S)/6-31G(d,p) and PBE0/LANL08(Pt)) of structural, thermodynamic, and reactive properties were performed. These results were used for adjustment of the ReaxFF force field parameters of Pt and H atoms. Using the adjusted parameters, the molecular dynamics simulations of the interaction between molecular and atomic hydrogen with the bare, chemically modified, and supported PtNPs were performed. It was found that the activity of the PtNPs in the molecular hydrogen dissociation decreases remarkable with the cluster size (see figure below). The cluster size is also the key parameter affecting the stability of PtNP against destruction in the hydrogen atmosphere. It was also demonstrated that the organometal ligands of different size (C_4H_9SH and $C_{12}H_{25}SH$) form different kinds of cluster coverage. This can lead to different mechanisms of regioselectivity onset which are realized on the PtNPs of different sizes and under different reaction conditions.



Hydrogen addition to Pt_n (n=24, 38, 116)

	Pt_{24} (FCC)	Pt_{38} (ESTOH)	Pt_{116} (TOH)
MD evolution time, ns	11.6	11.9	1.0
H_2/Pt_n collisions ($r < 3A$)	20896	32486	7913
Long-living complexes ($\tau > 10$ ps)	8	10	2
Dissociation probability	$3.8 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$
Number of surface Pt atoms	22	32	78
«Reduced» reaction probability (NP activity)	$1.7 \cdot 10^{-5}$	$0.97 \cdot 10^{-5}$	$0.32 \cdot 10^{-5}$

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PP-121

Synthesis of the catalyst of hydrofining fuel and oils with application of chelate complexes

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It is widely known that to raise the efficiency of process of hydrofining the distinct trend to simultaneous optimization of a structure of supporters and increase in the concentration of the active centres of strictly certain structure in catalysts hydrodesulfurization, namely «CoMoS-II» phase is observed. In the present work formation questions of alumkaolinborate supporters from the developed system of large pores from 6 to 10 nanometers for hydrodesulfurization of diesel fractions and more than 10 nanometers for vacuum gas oils and the residual oils are considered. Such structure provides accessibility of the active centers of the catalyst to the large molecules, which have been substituted for alkyldibenzothiophen, and resin- pyrobitumen substances which geometrical sizes attain from 7 to 10 nanometers. For the purpose of regulating of porous structure used various processing methods, including the variation of peptizing agents and replacement intermicellar liquids in the formed granules. Thus, supporters allowing in regular intervals have been synthesised to put moderate concentration of active components for one soakage, from the joint solutions stabilised by phosphoric acid.

Recently to obtain catalysts, active at the removal not only of sulphur, but nitrogen, the method of soakage of supporters is used by the solution of separately synthesised bimetallic complex compounds containing in the capacity of ligand of lemon acid ($C_6H_8O_7$ or its monohydrate – $C_6H_8O_7$ x H_2O), and also various oxygen-containing compounds. Therefore trying is undertaken to carry out synthesis of hydrofining catalysts by soakage, a joint multicomponent solution of salts of cobalt, nickel and molybdenum, stabilized mix of phosphoric and lemon acids. The complex of physical and chemical methods proves formation of chelate complexes, ions of transition metals in soakage solution, thus the basic part of molybdenum was in the composition of para- molybdate of anions. The catalyst offered by us has following characteristics – of 72 % of pores with Dcp from 7 to 11 nm, and by results of chemical analysis contains, weight %: Al_2O_3 – 70.57, SiO_2 – 6.39, B_2O_3 – 2.40, P_2O_5 – 0.73, CoO – 2.10, NiO – 0.70, MoO_3 – 15.2, C – 1.78, impurity the rest. The extent of removal of sulphur at test in microcatalytic installation at sulphurizing hydrogen sulphide made 98.9 % in the course of hydrofining of diesel fraction and 95.9 % in case of dewaxing residual fraction.

PP-122

Boehmite particles with the different morphology as a precursor of catalysts alumina support

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Boehmite is aluminum oxyhydroxide (γ-AlO(OH)) is widely used in industry as a precursor of alumina. It is transformed to γ-Al_2O_3 under heat treatment of 350-750 °C which is required for the production of petrochemical refining process catalysts, catalyst supports [1], adsorbents and desiccants [2], membranes and filters. Specific properties of the most important aluminum oxides based materials such as a specific surface area, pore volume, shape and size and the granules strength depend largely on the structural characteristics of its precursor (its size, morphology and character packing arrangement of boehmite particles) which in turn depend on the way it was synthesized.

X-ray diffraction, thermal analysis, laser diffraction, scanning electron microscopy, transmission electron microscopy, ^{27}Al nuclear magnetic resonance and low-temperature nitrogen adsorption method were used to understand the influence of hydrothermal (200 °C, 1.7 MPa) and heat (350 °C, atmospheric pressure) treatments of coarse gibbsite floccules (40-180 μm) on the morphology and particle size of the boehmite formed. Under the hydrothermal treatment of γ-$Al(OH)_3$ nonporous boehmite is formed with the specific surface area value of 1.3-3.4 m^2/g. In the "dry steam" conditions the floccules are broken while the plate-shaped γ-AlO(OH) particles are formed; lozenge- and block-shaped γ-AlO(OH) particles are crystallized into the cracked floccules in an aqueous suspension. These floccules are not destroyed in the heat and the following hydrothermal treatment. It is been established for the first time that the flaky-shaped γ-AlO(OH) particles are formed within the coarse floccules producing a laminated packaging film lozenge-shaped crystals which results in a 0.1 cm^3/g pore volume and 29 m^2/g specific surface area. The data obtained are of a high industrial importance in the area of producing materials based on the coarse boehmite floccules with different properties.

Acknowledgement. This work was supported by the Russian Government Program of Competitive Growth of Kazan Federal University.

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PP-123

Anion destruction driven mechanism of activation of air-tolerant, activator-free catalyst for alkenes di-/polymerization:[Pd(acac)(MeCN)$_2$]BF$_4$

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Transition-metal-catalyzed olefin oligomerization and polymerization reactions constitute one of the most important industrial processes for forming polyolefins and α-olefins. Oligomerization (and polymerization) catalysis typically involves either a sensitive organometallic precursor or activators such as aluminum alkyls. Aluminum alkyls free cationic Pd-catalyzed systems with O⌒O-chelating ligands (O⌒O = β-diketonates or carboxylates) have shown promising results for oligo- and polymerization of olefins. However, these Pd-catalyzed systems needed an additional Lewis acid such as $BF_3{\cdot}OEt_2$, In(OTf)$_3$ or Cu(OTf)$_2$ to generate active catalytic species. Recently we have reported that bench-stable [Pd(acac)(MeCN)$_2$]BF$_4$ (**1**) can be used as single component catalyst for substituted styrenes dimerization and norbornene polymerization including under air conditions. We were interested in elucidating the mechanism of this reaction. As generally believed, for both norbornene polymerization and styrene dimerization the active species is a Pd−H intermediate, it is worth noting that, two distinct pathways are possible for the insertion of the first molecule of substrate. The alkene can undergo migratory insertion into either a Pd−C bond (BF_3-assisted pathway) or a Pd−O bond (metallacycle ring expansion mechanism). In order to distinguish between these two pathways of the reaction, the DFT computational studies were performed at the BP86/def2-TZVP&def2-SVP level. It has been found that BF_3-assisted acetylacetonate activation is preferred both kinetically and thermodynamically. In the reaction mixture **1** and St ($[St]_0:[Pd]_0 = 4:1$) after 20 h in CH_3NO_2 two products with $m/z = 200$ (M^+), and 202(M^+) were observed by GC-MS that originate from one styrene insertion into the Pd−C bond of acetylacetonate ligand followed by β-hydride elimination.^{13}C-NMR spectrum of the same reaction mixture after 2 h showed complete set of signals of the transformed acac ligand (ppm): 204.4 (C=O, non-coordinated, keto-acac), 197.7 (BF_2(acac) fragment), 192.4, and 192.2 (C=O, non-coordinated, enol-acac). Interestingly, we have observed that solutions of **1** in $CHCl_3$, CH_2Cl_2, CH_3NO_2 decomposes partially after several hours with formation of black residue (in GC/MS spectra of the solutions BF_2(acac) was detected), while in solid state complex is air stable for months. Thus, it appears that the catalytic reaction is driven by anion destruction followed by attack of boron trifluoride to κ^2-O,O-acetylacetonate ligand bonded to palladium in **1** involving the formation of neutral palladium fluoride complex as activation by-product. Only few examples of tetrafluoroborate anion boron–fluorine bond activation, yielding a boron trifluoride were reported in literature for Zr and Ga complexes.

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PP-124

Influence of peripheral and non-peripheral substituents nature on catalytic properties of tetrapyrrolic macroheterocyclic cobalt complexes

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Catalytic properties provided by metal complexes of phthalocyanines are known for various organic reactions [1-2]. Commonly, catalytic processes involving metal phthalocyanines are based on coordinative interaction of reagents and catalyst accompanied by formation of intermediate complexes. State of phthalocyanine macrocycle coordination center is directly depended on electronic effects and sterical effects of substituents placed in annulated benzene fragments [3]. Introduction of functional fragments having different nature into peripheral and non-peripheral positions of metal phthalocyanines not only provides solubility in different solvents but also determines fine aspects of association behavior in liquid-phase systems. Green chemistry principals bring liquid-phase systems using water as a solvent to front.

Solubility of metal phthalocyanines may be reached through introduction of ionogenic groups, for example –SO_3H or –COOH, on periphery of the macromolecule.

Current work contains study on kinetics of N,N-carbamodithiolate and 2-mercaptoethanol oxidation in presence of symmetrically and bifunctionally substituted cobalt phthalocyanines bearing with sulfo- and carboxy-groups in conjugated and unconjugated monophenyl and biphenyl peripheral substituents. Kinetic equation obtained by using of formal Michaelis kinetics describes these systems for all investigated phthalocyanines with a good accuracy and has linearization in Lineweaver-Burk coordinates. These data suggest earlier proposed mechanism of oxidation process through formation of substrate-phthalocyanine-oxidizer triple complex [4-5]. There is compensation effect observed for symmetrically substituted phthalocyanines which caused by sterical factor of biphenyl peripheral substituents and H-aggregation processes.

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PP-125

Enantioselective Aerobic Oxidative coupling of *β*-Naphthols Catalyzed by Chiral Iron Complexes

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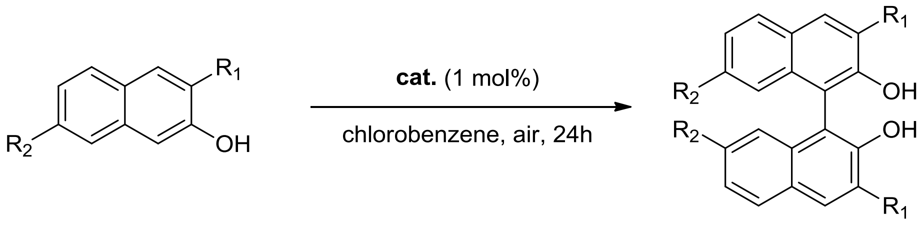
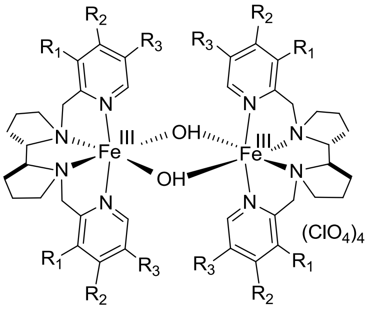
Optically pure 1,1’-bi-2-naphthols (BINOLs) have been widely used as chiral auxiliaries and ligands for asymmetric transformations. These compounds have also been used for preparation of organic materials such as organic light-emitting devices and chiral sensors [1]. The most attractive strategy for the synthesis of optically pure BINOLs is direct oxidative coupling of β-naphthols in the presence of chiral catalysts [2].

In this work, a series of chiral iron(III) aminopyridine complexes have been prepared and tested in the aerobic oxidative coupling of substituted β-naphthols. Upon 1 mol. % catalyst loadings, these complexes ensure moderate to good yield of the corresponding BINOLs (up to 87 % within 24 h), having up to 53 % optical purity. The effect of ligand substitutents, solvent, counteranion, β-naphthol structure, and oxygen pressure on the catalytic performance has been systematically examined.





a: R_1,R_3= CH_3; R_2= OCH_3;
b: R_1= CH_3; R_2= CH_2CF_3; R_3= H;
c: R_1, R_2, R_3= H;

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, project 16-29-10666.

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PP-126

Hidden radical reactivity of the $[FeO]^{2+}$ group in the H-abstraction from methane by iron (hydro)oxide species

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The $[FeO]^{2+}$ group in the ferryl S=2 $Fe^{IV}=O$ ground state is shown to be key intermediate in the oxidation catalysis by the non-heme iron enzymes and by the FeZSM-5 species called Panov's alpha-oxygen. The electron configuration of the $[FeO]^{2+}$ group in various ligand surrounding is usually of the ferryl type $Fe^{IV}=O$ and only the ligand-to-metal charge transfer excited state possesses the oxyl $Fe^{III}\text{-}O^{\bullet}$ character. With the use of model iron-hydroxide complexes we showed that hydrogen abstraction from methane is determined by the $Fe^{III}\text{-}O^{\bullet}$ excited state. For some ferryl surrounding like that in the tetramer $Fe_4O_5(OH)_3$ this center becomes as active as gaseous OH radical. This reveals an effect of the "hidden" first excited oxyl state $Fe^{III}\text{-}O^{\bullet}$.

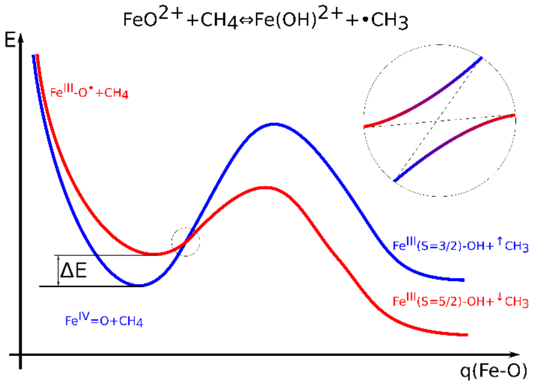

Figure 1. Ferryl-oxyl avoided crossing for the reaction $FeO^{2+} + CH_4 \rightarrow Fe(OH)^{2+} + {\bullet}CH_3$.

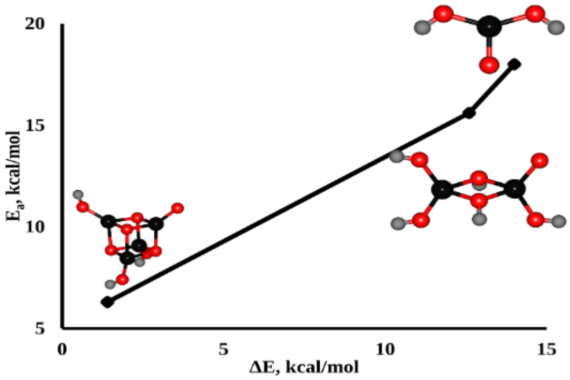

Figure 2. Correlation between the energy of the oxyl-ferryl gap and the activation energy of the H-abstraction from methane.

The crossing of the ferryl and oxyl terms having the same symmetry in the H abstraction process is explained qualitatively in terms of the avoided-crossing mechanism. (Figure 1) One of the sequences of this mechanism is that the activation energy correlates with the energy of the ferryl-oxyl gap: the smaller gap, the lower activation energy. (Figure 2)

Since the above-considered H-abstraction process takes place on a terminal oxygen alone, presented qualitative conclusions seems to be applicable to any S=2 ferryl group.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.45.3.6).

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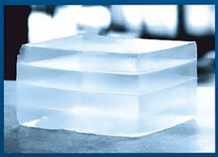

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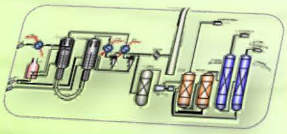

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CONTENT

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